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INDUSTRIAL CHEMISTRY

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Edited by SAMUEL RIDEAL, D.Sc. (Lond.), F.I.C., Fellow of University College, London.

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THE CHEMICAL INDUSTRIES

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THE
ALKALI INDUSTRY

BY

J. R. PARTINGTON, D.Sc. (Vict.)

ASSISTANT IN THE CHEMICAL DEPARTMENT, UNIVERSITY OF MANCHESTER

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GENERAL PREFACE

The rapid development of Applied Chemistry in recent years has brought about a revolution in all branches of technology. This growth has been accelerated during the war, and the British Empire has now an opportunity of increasing its industrial output by the application of this knowledge to the raw materials available in the different parts of the world. The subject in this series of handbooks will be treated from the chemical rather than the engineering standpoint. The industrial aspect will also be more prominent than that of the laboratory. Each volume will be complete in itself, and will give a general survey of the industry, showing how chemical principles have been applied and have affected manufacture. The influence of new inventions on the development of the industry will be shown, as also the effect of industrial requirements in stimulating invention. Historical notes will be a feature in dealing with the different branches of the subject, but they will be kept within moderate limits. Present tendencies and possible future developments will have attention, and some space will be devoted to a comparison of industrial methods and progress in the chief producing countries. There will be a general bibliography, and also a select bibliography to follow each section. Statistical information will only be introduced in so far as it serves to illustrate the line of argument.

Each book will be divided into sections instead of chapters, and the sections will deal with separate branches of the subject in the manner of a special article or monograph. An attempt will, in fact, be made to get away from the orthodox textbook manner, not only to make the treatment original, but also to appeal to the very large class of readers already possessing good textbooks, of which there are quite sufficient. The books should also be found useful by men of affairs having no special technical knowledge, but who may require from time to time to refer to technical matters in a book of moderate compass, with references to the large standard works for fuller details on special points if required.

To the advanced student the books should be especially valuable. His mind is often crammed with the hard facts and details of his subject which crowd out the power of realizing the industry as a whole. These books are intended to remedy such a state of affairs. While recapitulating the essential basic facts, they will aim at presenting the reality of the living industry. It has long been a drawback of our technical education that the college graduate, on commencing his industrial career, is positively handicapped by his academic knowledge because of his lack of information on current industrial conditions. A book giving a comprehensive survey of the industry can be of very material assistance to the student as an adjunct to his ordinary textbooks, and this is one of the chief objects of the present series. Those actually engaged in the industry who have specialized in rather narrow limits will probably find these books more readable than the larger textbooks when they wish to refresh their memories in regard to branches of the subject with which they are not immediately concerned.

The volume will also serve as a guide to the standard literature of the subject, and prove of value to the consultant, so that, having obtained a comprehensive view of the whole industry, he can go at once to the proper authorities for more elaborate information on special points, and thus save a couple of days spent in hunting through the libraries of scientific societies.

As far as this country is concerned, it is believed that the general scheme of this series of handbooks is unique, and it is confidently hoped that it will supply mental munitions for the coming industrial war. I have been fortunate in securing writers for the different volumes who are specially connected with the several departments of Industrial Chemistry, and trust that the whole series will contribute to the further development of applied chemistry throughout the Empire.

SAMUEL RIDEAL.

AUTHOR'S PREFACE

CHEMISTS and engineers who are interested in the alkali industry are fortunate in having at hand such a treatise as the classical work of Lunge, on "Sulphuric Acid and Alkali." This book, which contains a detailed account of the industry, is a mine of information, and makes detailed references to the older literature superfluous. It is directed, however, chiefly to the engineering and technical side of the subject, and is also by reason of its size hardly suitable for students wishing to obtain a bird's-eye view of the subject, especially in its relations to pure science. A really scientific interpretation of the various processes used on a large scale is not in fact very prominent in the larger treatises. The chief points which the author of the present work has kept in view have therefore been to give a concise and connected sketch of the whole subject, and always if possible to give some explanation for the mode of procedure adopted in each case. In this way it is hoped that the book may be regarded as an introduction to, and also as supplementing, the larger and more technical treatises, and that it may also be of some interest to the technical expert who wishes to keep in touch with the recent applications of pure science to the industry. It should also be useful to teachers of Chemistry.

It is true that our knowledge on various fundamental questions is still very imperfect, but this has resulted largely from the fact that the need for such information has not been altogether clearly perceived by the technologists, who have therefore failed to enlist the interest of workers in the scientific laboratories. There is also some truth in the surmise that some of the problems which are proposed to chemists by practical men resemble the famous one propounded by the amateur scientist Charles II: "Why does a dead goldfish when put into a bowl of water cause the water to run over, whilst a live goldfish does not?" Some technical recipes doubtless contain elements of unverified difficulty. In other cases the complete elucidation of the problem requires more data than we at present possess—a striking instance is the chemistry of the Weldon chlorine process. The necessary data are partly purely chemical and partly measurements of the changes of available energy in the processes, which latter have the significance formerly, and even still erroneously, attributed to the heats of reaction.

It was therefore necessary to give an extremely brief account of the modern thermodynamic measurement of affinity, and to illustrate its application in one or two instances. There is a rich field open for experimental work in this direction.

Of more importance than the explanation of the known is the creation of new knowledge, especially as the working conditions essential to the success of a process have usually to be determined in each case *de novo*. In this branch of technical research the law of mass action and the principles of thermodynamics have played a prominent part, and the treatment has therefore included these two branches of physical chemistry. This branch of modern chemistry has not in this country received the attention it merits and enjoys in lands where chemical industry is making more progress than was formerly the case here.

The author has endeavoured to follow the excellent general scheme of the series laid out by the Editor in his introductory remarks. Special attention has been paid to the resources and needs of the British Empire, and possible future independence of German supplies (*e.g.* in the potash industry). Particular attention has been given to modern processes of Nitrogen Fixation, as far as they concern the present volume. Questions of costs and statistics have not been emphasized; the experts on this side are rarely in agreement, and the figures as given are usually unreliable. In any case they will no doubt be considerably modified in the course of a year or two. Such figures as are given, especially in connection with Nitrogen Fixation, are believed to be reliable.

The diagrams have been drawn by Mr. G. J. Jones, A.R.C.Sc.I., and the author has great pleasure in recognizing his valuable assistance.

The references to the literature do not aim at completeness. It appeared preferable to make a careful selection of publications which themselves contain complete references to earlier literature, and thus save much space. All references have been verified, and placed at the end of each section, where they are not an annoyance to the reader. It is hoped that this plan may have some advantages over the one which appears to be coming more into use, of scattering numerous references, mostly unverified, throughout the text itself.

The author would value criticism, or additional information from those actually engaged in the industry, with a view to improvement of future editions.

J. R. P.

February, 1918.

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ALKALI INDUSTRY

INTRODUCTION

The Alkali Industry in Great Britain.—The manufacture of soda, and the allied industries of Sulphuric Acid, Chlorine, and Bleaching Powder, have during the nineteenth century acquired an immense importance in the industries of Great Britain, the production per head of population being still the highest in the world, although the United States have recently become the largest nett producers. In this respect the peculiar advantages offering themselves in Great Britain, by the occurrence of the materials required in the industry within easy access, make the so-called " Heavy Chemical Industry "—chiefly sulphuric acid and alkalies—of the greatest importance, and this position is likely to be maintained, if not considerably improved, when the readjustment necessary after the war has been effected. The case is quite otherwise with the " Fine Chemical Industry." This, which comprises chemicals in a state of purity, synthetic drugs, and colours, has largely passed into German hands, the first branch notably to firms such as Kahlbaum, and Merck, the latter to the immense combines known as Friedrich Bayer and Co. and the Anilin und Soda Fabrik. There is no industrial or economic reason why such products should not be made in Great Britain, because the necessary raw materials (*e.g.* coal-tar) exist here in abundance. The reason why the colour industry, for example, has largely passed out of our hands is probably more likely to be sought in the attitude shown in the country to chemical research and scientific chemistry in general during the years in which Germany has been building up her great chemical industry.

This lack of encouragement of scientific chemistry has prevented any effective co-operation of chemists with manufacturers, without which the latter must necessarily fall behind their more enlightened competitors, who have at their disposal the latest results of modern science. Since the vital importance of chemical industry has been so drastically brought home by the war to manufacturers, and indeed to the public at large, it is hoped that some change will follow, and the chemical industry of the country put on a more secure basis than previously. Unless chemical research goes hand-in-hand with the new industry, the complete failure of attempts to produce fine chemicals, such as aniline dyes, drugs, or pure chemicals, may be awaited with certainty from the start. The problems confronting chemical industry in this country are less engineering than purely chemical, and scientific chemistry of a much higher standard than has usually satisfied manufacturers is the only thing which can put the new industry on a firm and enduring basis. It will be a mistake to suppose that a mixture of elementary chemistry and engineering will be the necessary equipment for the industrial chemists of the future; it is a much more extensive knowledge of chemistry which will be the first necessity of the technical chemist.

The Site of the Alkali Works.—The position for an alkali works is regulated chiefly by the conditions that a plentiful supply of raw materials must be available in the vicinity, and that facilities for transport exist. In other words, the points to be considered are mainly raw materials and freights. The raw materials are Coal, Salt, and Limestone, with Pyrites for the Leblanc process, and Ammonia for the Ammonia-soda process.

The simultaneous occurrence of the three first-named materials has fixed the important alkali works in Lancashire, Cheshire, and the Tyneside. Whole towns are practically entirely devoted to the alkali industry, and the appearance of such "Alkali Towns" is familiar in the north of England. If we consider Widnes and Northwich as representative of the Leblanc and Ammonia-soda processes respectively, we have before us typical alkali towns. The rows of chimneys emitting black smoke from the unscientific combustion of coal, the enormous lead chambers, towers, revolving furnaces, waste heaps, with the escaping steam, the noise, and the smell of acids, chlorine, and sulphuretted hydrogen, are all familiar. These are in marked contrast to such a works as that of Cheddes, in the Alps, where water-power and electrolytic processes are used, and one is struck by the elegant buildings, clean and almost silent, which are quite unlike the usual alkali works. In this country the engineer is confined to the use of carbonaceous fuel, but this is often burnt in the most inefficient possible way, and the valuable by-products, such as tar and ammonia, are wasted. The use of water-power can never become extensive in the British Isles, although the utilization of the Falls of Foyers by the British Aluminium Company has been successful, and even in America, where water-power is abundant, the price is not so low compared with fuel as it was at first, owing to the inevitable financial manipulation of the use of a perfectly free natural source of power when once its value has been demonstrated. The use of producer-gas plants, with recovery processes, and possibly the gasification of peat, of which immense supplies exist in Ireland, together with central power-station schemes, may do much in future in the way of providing cheap sources of power. In many cases the success or otherwise of a process will depend entirely on the possibility of cutting down the power costs to a minimum. In any case, one may expect increasing competition to draw the attention of manufacturers to these problems. Incidentally, it may be mentioned that the Castner-Kellner Alkali Company at Runcorn utilize Mond gas-producers in connection with an electric power station to generate the electrical energy required for the production of electrolytic alkali, and apparently with complete success.

The railways and inland waterways are of the greatest importance in fixing the site of an alkali works, and indeed of a works of any kind. As an instance one may consider the supply of limestone from Buxton to the Northwich works by the Midland Railway, and the proximity of the great Crewe junction of the London and North Western line, as well as the facilities for water-borne transport on the River Weaver, which communicates with the Manchester Ship Canal at Runcorn, and the Mersey at Liverpool. Northwich is in effect an inland port, and has a shipbuilding industry. Similar facilities are found at Fleetwood in Lancashire, and on the Tyne.

The Future of the Alkali Industry.—If we consider the main problems and factors which will determine what is to be the future of each of the branches of the alkali industry, we can probably say that the utilization of the Natural Soda deposits of British East Africa depends chiefly on transport and freights; that of the Leblanc process on the cheapness of sulphuric acid and the demand for chlorine and bleaching-powder; whilst the problems confronting the Ammonia-soda and Electrolytic processes respectively are the utilization of the chlorine lost from the salt as calcium chloride in the former, and the cheap supply of electrical energy in the latter. The energy problem does not mean the supply of water-power, as we have already indicated.

Besides the soda industry, the question of potash supplies is one which will demand careful and urgent consideration, as the complete dependence on Stassfurt which characterized pre-war conditions will no longer be tolerable. The United States indeed began to investigate this matter some years ago, and are apparently on the way to a satisfactory solution; it should be faced in this country without further delay. If the schemes of increased agricultural output are ever to materialize, the supply of fertilizers, including nitrates and potash, for both of which we are at present solely dependent on foreign countries, will have to be assured. The problem, as usual, comes back to chemistry.

The Alkalies.—It was not until 1737 that the difference between potash, obtained by the lixiviation of wood-ashes, and soda, the base of common salt, was pointed out by the French chemist Duhamel. This difference was denied by Pott, but was finally confirmed by Margraaf, who discovered the flame reactions, and the reactions with platinic chloride, of the two alkalies. Kunkel (*d.* 1702) had referred to caustic ammonia; the carbonate had long been known under the name of spirit of hartshorn, and was prepared by the destructive distillation of bones, horn, etc.

The true nature of the alkalies was however largely elucidated by the classical researches of Joseph Black (1752). In his time three alkalies, and a "mild" and "caustic" form of each, were known:—

(1) Mild Vegetable Alkali (K_2CO_3), obtained by lixiviating wood-ashes. By treatment with lime this gave Caustic Vegetable Alkali (KOH).

(2) Mild Marine Alkali (Na_2CO_3), obtained in Normandy by the lixiviation of ashes of seashore plants. With lime this gave Caustic Marine Alkali (NaOH).

(3) Mild Volatile Alkali ($(NH_4)_2CO_3$), obtained by the destructive distillation of bones, and giving Caustic Volatile Alkali (NH_4OH) with lime.

According to the Phlogistic Theory then in vogue, limestone on burning absorbs phlogiston, ϕ, from the fire, and this phlogiston was regarded as the "principle of causticity":—

$$\text{Limestone}+\phi=\text{Quick—or caustic—lime}$$
$$\text{Mild alkali}+\phi=\text{Caustic alkali}$$

The process of caustification of mild alkalies by lime was regarded as a transfer of phlogiston from the lime to the alkali:—

$$(\text{Limestone}+\phi)+\text{mild alkali}=\text{Limestone}+(\text{mild alkali}+\phi)$$

Black, however, showed that causticity is due to the loss of "Fixed Air" (CO_2), because on heating limestone there is a loss of weight, and fixed air is disengaged. If the quicklime formed is dissolved in water and treated with mild alkali, a weight of limestone equal to the original is obtained; it had therefore been exactly re-formed by taking fixed air from the mild alkali, leaving the latter caustic:—

$$CaCO_3=CaO+CO_2$$
$$CaO+H_2O+K_2CO_3=CaCO_3+2KOH$$

The same fixed air was obtained by the action of acid on mild alkali as by the action of acid on limestone, and the solution of limestone in acid gave the original weight of limestone when precipitated with mild alkali :—

$$CaCO_3+2HCl=CaCl_2+CO_2+H_2O$$
$$K_2CO_3+2HCl=2KCl+CO_2+H_2O$$
$$CaCl_2+K_2CO_3=CaCO_3+2KCl$$

Up to the time of Davy, the caustic alkalies were regarded as elements. In 1807, however, that chemist succeeded in decomposing the fused alkalies by means of an electric current, producing for the first time the metals potassium and sodium by a method now used on a large scale for their manufacture.

Lithium salts were discovered by Arfvedson in 1817, and the metal isolated by Bunsen and Matthiessen in 1855.

The rare alkalies cæsia and rubidia were discovered by Bunsen in 1860, during a spectroscopic examination of certain rare minerals.

Many substances other than the alkalies proper give reactions which are regarded as characteristic of alkalinity, viz.—

(1) They have a soapy feel, and a corrosive action on the skin.
(2) They restore the colours of various dyes, which are changed by acids (litmus, methyl orange, etc.), and also give colour reactions of their own (juice of violets, turmeric, phenolphthalein, etc.).
(3) They neutralize the acids to form salts.

Thus, the alkaline properties are possessed by the so-called Alkaline Earths, lime, baryta, and strontia, and in a less degree by many other substances in aqueous solution, such as sodium carbonate, borax, trisodium phosphate, etc. The cause of these alkaline properties has been traced to the Hydroxyl ion, OH', and since the alkalies are electrolytically dissociated very largely into cations and hydroxyl ions, they are the alkalies *par excellence.*

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SECTION 1.—THE SALT INDUSTRY

Common Salt; Sodium Chloride, NaCl.—Sodium chloride has been known from the earliest times. It is very widely distributed, occurring in small quantities in all the primary (*i.e.* non-stratified) formations of the crust of the earth. From these it has passed by the action of water to rivers, and thence to the sea. The deposits of salt found in many localities have been produced by the evaporation of former seas and lakes.

Rock Salt occurs in many places in Europe, Asia, Africa, and America. Thus at Wielicza (Carpathians) there are beds 1200 ft. thick, which have been worked since the eleventh century, and the product, as obtained by blasting, is almost pure NaCl. In Cardona, in Spain, there are two hills of rock-salt each a mile in circumference. In Russia the richest deposits in the world occur at Iletzky Zastchit, on the left bank of the Ural, in the province of Orenburg; these are 3 sq. km. in area and 140 m. thick. There are also deposits in Astrakhan, the Caucasus, Kars, Ekaterinoslav, and the Trans-Caspian province. In Germany the Staussfurt deposits, near Magdeburg, are important, the layers being 3000 ft. thick at a depth of 830 ft. Deposits occur in the Alps (*e.g.* at Salzburg), and there are twenty mines in Sicily. Deposits occur in the Vosges district (Lorraine), near Nancy in France, and in China, Africa, Mexico, Venezuela, and the United States (New York, Michigan); in Manitoba and Athabasca in Canada; in India, where there are very pure rock-salt hills in the Punjab, and at Kohat, and Mandi. In the British Isles the first deposit of rock-salt was discovered at Marbury, near Northwich, in Cheshire, in 1670. Many other deposits were found in this district, the richest being at Northwich and Winsford. The Cheshire beds are in the upper Trias formation, probably identical with the "Bunter" Sandstone of Stassfurt. The top salt-bed at Northwich is 135–150 ft. below the surface, is 75 ft. thick, and is followed by the second bed of 105 ft. thickness after an interval of 30 ft. of hard marl. After this successive thin beds occur. Deposits also occur in Lancashire, near Barrow-in-Furness; at Droitwich and Stoke Prior in Worcestershire; and in Ireland at Carrickfergus, and near Larne.

The Cheshire Salt Industry.—The preparation of salt from brine springs (as distinguished from rock-salt) was carried on in Cheshire during the Roman occupation of Britain, lead pans containing only a few gallons being used. With the difference that iron pans holding several thousand gallons of brine are now used, the modern process of salt-making carried on in Cheshire is almost the same as that of the Romans. A shaft of 10 ft. diameter is sunk to the marl, and the latter tapped by a bore-hole. If no natural brine is found, water is let down; the dense brine formed sinks and is pumped from the bottom through large iron pipes to the works. More water flows in, and large cavities are produced, often causing serious subsidences of land in the district. The effect of these subsidences may be seen at any time in Northwich, where houses or rows of houses often tilt over and are sometimes destroyed.

The composition of Northwich brine is usually :—

Sodium chloride	25·790 per cent.
Calcium sulphate	·450 ,, ,,
Magnesium chloride	·093 ,, ,,
Calcium carbonate	·018 ,, ,,
Calcium chloride	·044 ,, ,,
Water	73·605 ,, ,,

In Germany weaker brines often occur, and a preliminary concentration by spraying over stacks of twigs exposed to prevailing winds—so-called "Graduation"—is sometimes used.

The brine is boiled down in *salt pans*, made of boiler-plate riveted together with angle-irons, set up over brick-work flues and fired from below with coal. The pans are all placed over the same flue, the smaller ones (25 ft. by 20 ft. by 1¼ ft.) being nearest the fire. In these the evaporation is carried on rapidly at 107·5° C., the fine salt separating being raked to the side of the pan by the workman using a perforated spade, or "skimmer." Every 8–12 hours the salt is withdrawn, put into moulds of wood and cooled. In this way the mother liquors crystallize and bind the whole together into *lump-salt*, the blocks of which are knocked out of the moulds. *Table salt* is produced by grinding these, or by draining the separated fine crystals. To prevent deliquescence, due to magnesium chloride, a phosphate may be added ("Cerebos salt"). In Germany the salt is dried by centrifugals, and placing in a rotating copper cylinder lined with cement, through which hot air passes. If moist salt is stacked in heaps exposed to bright sunlight, hypochlorous acid is produced by photochemical action, and this would give a peculiar flavour to the salt.

Following the small pans come those of intermediate size (40 ft. by 25 ft. by 1½ ft.), in which the evaporation occurs at 60°–80° C., with the production of coarser-grained *manufacturers' salt*, which is taken out every 24–48 hours, and shipped or put into railway trucks.

Fishery Salt is of still coarser grain, and is used in fish curing. It is produced by evaporation at 38°–60° C. in larger pans (60 ft. by 25 ft. by 2 ft.), and removed every 7–14 days. The addition of alum favours the production of larger crystals, doubtless by precipitating the colloidal substances in the brine, the presence of which favours the production of small grains. Conversely, glue and grease are sometimes added in small amounts to promote deposition of fine-grained salt. This action is similar to the promotion of a smooth deposit of metal in electro-deposition by the addition of colloids such as glue, and probably is due to the formation of a colloid layer over the very small crystals, which prevents further growth.

In the largest pans (135 ft. by 30 ft. by 2 ft.) the evaporation is carried out at 40°–50° C., with formation of large crystals of *Bay salt*, usually in the form of floating "hoppers," which are removed every month. The waste flue gases then pass to low chimneys.

During evaporation the calcium carbonate separates as a "sand scale," and the calcium sulphate as a hard adherent "pan scale." The pans are therefore cleaned, or "picked," occasionally.

Multiple-effect Evaporators.—In 1839 John Reynolds proposed the use of vacuum pans for evaporation of brine. At first much trouble was caused by the deposited gypsum choking the pipes. The brine is now first purified by adding milk of lime, followed by ammonium carbonate :—

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 \text{ ppt.} + CaCl_2$$
$$CaCO_3 . CO_2 + CaO = 2CaCO_3 \text{ ppt.}$$
$$CaSO_4 + (NH_4)_2CO_3 = CaCO_3 + (NH_4)_2SO_4$$
$$CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl$$

The ammonia is afterwards recovered from the mother-liquors by adding lime and distilling.

The brine so purified is run into *closed pans*, and the steam generated in the first pan by steam coils or flue gases passing through coils, is carried to coils in the second pan, the steam generated in which passes in turn to the third pan. With three pans, the system is called a Triple Effect Evaporator (Fig. 1), and so on. The vacuum is maintained by a pump P communicating with the last pan A_1, which is thus under the lowest pressure, and in which evaporation occurs at the low temperature of the steam from the previous pan A_2. The pressure increases to the first pan A_3, and the boiling points are progressively higher. A very long leg is attached to each pan, so that the vacuum is balanced by the column of brine. The salt separating in the pan falls down the leg to an open vessel, from which it is elevated to a hopper. After draining in a centrifuge it is 99·8 per cent. NaCl.

In the process of Vis (1898) the $CaSO_4$ is precipitated in small crystals, which mix with the salt, by adding $CaCl_2$ to the brine. (This precipitation process is an example of the law of mass action, of which similar cases are fully considered

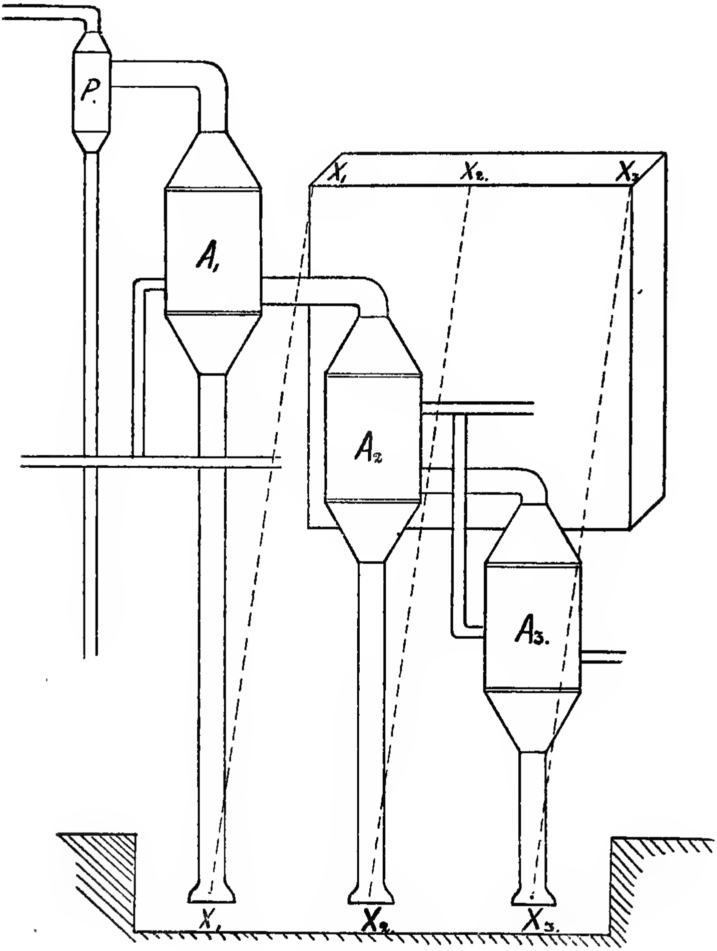

FIG. 1.—Vacuum Salt Pans.

at a later stage in connection with caustic soda, and the ammonia-soda process, pp. 76, 85.) The salt is washed free from $CaCl_2$ by fresh brine, and the washings sent with the brine feed to the evaporators, so that the same $CaCl_2$ can be used over and over again.

In ordinary pans 1 ton of coal slack (15–20 per cent. ash) will produce 2 tons of salt at the rate of 15–20 tons per 24 hours. In triple-effect pans the same coal produces 5–6 tons of salt at the rate of 500–700 tons per 24 hours. The chief working cost, viz. fuel, is thus reduced, but the capital cost of plant is much higher than with the old direct-fired pans. Vacuum pans are being used in the Cheshire district at Winsford and Middlewich. They are largely used at Stassfurt, but of a slightly different type.

Solar Salt.—Large quantities of salt are obtained by the evaporation of sea-water, that of the Atlantic and Mediterranean containing about 3 per cent. NaCl, together with salts of magnesium, potassium, and calcium in smaller quantities. The Baltic and Black Seas are poorer in salt, whilst the Dead Sea contains 8 per cent., and the Great Salt Lake of Utah 20 per cent. NaCl.

In sunny climates the solar heat is used to evaporate sea-water. Thus there are 25 works at the mouth of the Rhone and in the Giraud district, and several in Italy and Sicily, where over 200,000 tons are produced annually. Deposits of salt in various parts of the world show evidence of deposition from natural inland lakes. In France and Italy *solar salt* is prepared by puddling a space of flat ground on the coast with clay and dividing it up into flat and very large basins called salt meadows. The sea-water enters the first at high tide and deposits clay, gypsum, etc. It is then run into the second pond, where by evaporation its specific gravity rises to 25° Bé., *i.e.* 25 per cent. NaCl, and pure salt is deposited in this "concentrating pond." The remaining liquor is concentrated in successive basins, called "crystallizing ponds," where at 27° Bé. a 96 per cent. NaCl is deposited. In further ponds a salt containing magnesium sulphate separates, called *sel mixte*, which is dissolved in water and frozen, when Glauber's Salt, $Na_2SO_4.10H_2O$, separates, leaving $MgCl_2$ in solution. In the last basin carnallite, $KCl.MgCl_2.6H_2O$, separates and is worked for

KCl. The final mother-liquors are treated to recover bromine and iodine by Balard's process (see p. 287). One sq. metre will produce 55–72 kg. salt in a good season. Vacuum pans have now been installed at Giraud. In Russia (Siberia and the North) sea-water is frozen, when pure ice separates. The concentrated salt solution is then boiled down.

Lee's Process.—Lee, on behalf of the International Salt Company at Carrickfergus, Ireland, proposed in 1903 to prepare pure salt from rock-salt by fusion in a special furnace. The salt, which melts at 815° C., flows away from the gypsum, etc., and may be ground and sold directly. It is claimed that 12 tons of salt are obtained per ton of coal, with a conversion cost of 2*s.* 6*d.* per ton.

Statistics of Salt Production.—The total production of salt in Great Britain in 1907 was 1,979,000 tons, valued at £644,000.

The productions in other countries about the same time were as follows :—

United States ..	3,000,000 tons.
Germany	1,841,000 tons (29,000 tons residues).
Russia	1,800,000 tons.
France	1,200,000 tons (50 per cent. from sea-water).
Italy	473,857 tons.
Austria	340,000 tons with $7\frac{1}{2}$ million hectolitres of brine.
China	1,648,000 tons.

In 1896 the world's production of salt was over 13 million tons, and this has probably increased of late. Salt is therefore the basis of the world's industries.

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SECTION 2.—SULPHURIC ACID

The Chamber Process.—Previous to 1740, sulphuric acid was exclusively prepared by distilling ferric sulphate, obtained by weathering pyrites-shale :—

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

This industry later on was directed mainly to the preparation of fuming acid, $H_2S_2O_7$, the manufacture being confined to the firm of Starck, in Bohemia. It was given up in 1900.

In 1740, however, Dr. Ward of Richmond introduced the process of deflagrating a mixture of sulphur and nitre, contained in an iron dish set over a pot of water under a large glass bell. The fragile glass vessels were replaced by Roebuck, at Prestonpans, in 1746, by lead chambers 2 metres wide, and the size of these was gradually increased. They were used in France in 1769, and in 1774 La Folie employed a steam jet in the chamber. A considerable advance was possible after the work of Clément and Désormes in 1793, who pointed out the importance of a current of air in the chambers, and in 1806 these two chemists gave a correct interpretation of the reactions occurring in the process.

The use of iron pyrites, FeS_2, as a cheap source of sulphur, introduced by Hill of Deptford, in 1818, and the invention of the Gay Lussac and Glover Towers, in 1835 and 1859 respectively, rounded off the already important chamber acid industry.

The magnitude of the industry, and its expansion in recent years, is well shown by the following table giving the weights of pyrites in 1000 tons, consumed in the different countries :—

Year.	England.	France.	Russia.	Germany.	America.
1900	753	397	—	627	536
1902	620	423	—	647	645
1904	753	426	—	678	620
1906	770	589	—	776	858
1908	777	592	—	878	890
1910	810	—	—	1008	1007
1912	—	—	256	916	—
1915	—	—	—	—	1359

The quantities of acid produced in 1910 by England, Germany, the United States, and Russia, were respectively 1,073,000 tons, 1,350,000 tons, 1,349,000, and 200,000 tons. In 1908 Italy produced 500,000 tons of acid. The production of acid has considerably increased during the last two years.

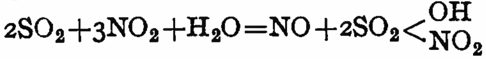
The roasting of pyrites and blendes in the Ural district in Russia would provide sulphuric acid for treatment of the rich phosphate deposits found there: the question of artificial fertilizers has lately become acute in that country.

The larger proportion of acid is still (1918) made by the chamber process, even in countries such as Germany, where the newer contact process has been largely introduced.

The chamber process is briefly as follows :—

Sulphur dioxide, mixed with excess of air, is produced by burning sulphur, pyrites, or other sulphide in suitable kilns. The hot gases pass over pots containing nitre and sulphuric acid, placed in the flues of the burners (or else nitrous fumes are produced in other ways), and then pass up the Glover tower, down which streams a mixture of weak chamber acid, and "Nitrous vitriol" obtained from the Gay Lussac tower. The nitrous vitriol is decomposed and oxides of nitrogen pass along with the sulphur dioxide, air, and some steam formed by the evaporation of the weak acid, to the series of lead chambers, where steam, or water spray, is blown in, and the reactions leading to the formation of sulphuric acid occur. The dilute acid falls as a spray to the floor of the chamber. The acid issuing from the Glover tower is fairly concentrated, and passes to the concentrating plant. The oxides of nitrogen are recovered from the gases at the end of the chambers by passing up the Gay Lussac tower, down which strong sulphuric acid trickles. They dissolve in this acid, producing nitrous vitriol (which is a solution of $\mathrm{SO_2}<{}^{\mathrm{OH}}_{\mathrm{NO_2}}$, nitrosulphonic acid, in sulphuric acid), and re-enter the cycle of changes when the latter is decomposed in the Glover tower. Fresh oxides of nitrogen must, however, be added to make up for loss.

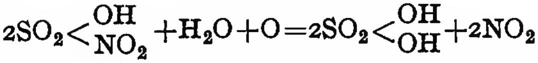
The theory of the chamber process has occupied the attention of chemists from the beginning of the last century to the present day. In 1806 Clément and Désormes had already recognized that the nitrogen oxides took part in the reaction; they, and later on Davy (1812), suggested the following cycle of changes :—

(1) 

$$\mathrm{2SO_2+3NO_2+H_2O=NO+2SO_2}<{}^{\mathrm{OH}}_{\mathrm{NO_2}}$$

Nitrosulphonic acid is in fact produced in white crystals if insufficient steam is admitted ("Chamber crystals").

$$(2) \qquad \mathrm{NO+O=NO_2}$$

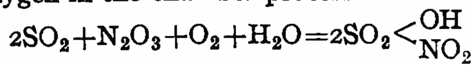
(3) 

$$\mathrm{2SO_2}<{}^{\mathrm{OH}}_{\mathrm{NO_2}}\mathrm{+H_2O+O=2SO_2}<{}^{\mathrm{OH}}_{\mathrm{OH}}\mathrm{+2NO_2}$$

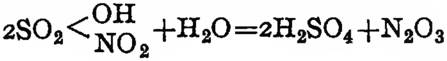
Lunge and Naef (1884–5), by analyzing chamber gases, found that in the first chamber (slightly red) NO is present in excess; in the other chambers (dark red) NO and NO_2 are present in equivalent proportions, and this mixture behaves chemically as N_2O_3 :—

$$\mathrm{NO_2+NO}\rightleftarrows\mathrm{N_2O_3}$$

These investigators claimed that N_2O_3 is therefore the carrier of oxygen in the chamber process :—

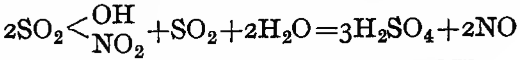
(1) 

$$\mathrm{2SO_2+N_2O_3+O_2+H_2O=2SO_2}<{}^{\mathrm{OH}}_{\mathrm{NO_2}}$$

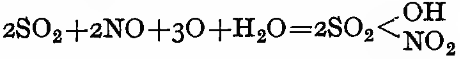
(2) 

$$\mathrm{2SO_2}<{}^{\mathrm{OH}}_{\mathrm{NO_2}}\mathrm{+H_2O=2H_2SO_4+N_2O_3}$$

The above are the main reactions. In the first chamber the nitrosulphonic acid reacts with SO_2, and NO (colourless) is produced, which then reacts with more SO_2 :—

(3) 

$$2SO_2{<}^{OH}_{NO_2}+SO_2+2H_2O=3H_2SO_4+2NO$$

(4) 

$$2SO_2+2NO+3O+H_2O=2SO_2{<}^{OH}_{NO_2}$$

Various other theories, introducing hypothetical intermediate compounds, have been proposed, but they appear to have less experimental foundation than Lunge's theory. The use of ultra-violet light has also been proposed to accelerate the chamber reactions.

Sources of Sulphur.—The sulphur dioxide introduced into the chambers is obtained mainly from the following sources, in decreasing order of importance :—

(1) Pyrites, FeS_2, sometimes containing CuS ;
(2) Native sulphur, or brimstone ;
(3) Zinc blende, ZnS ;
(4) Alkali-waste, from which sulphur is recovered by the Chance-Claus process ;
(5) Spent-oxide (Fe_2O_3 with up to 60 per cent. sulphur) from gas-works.

Iron Pyrites (FeS_2, 53·33 per cent. S).—Spanish and Norwegian pyrites, containing about 49 and 40 per cent. sulphur, respectively, are the richest. Pyrites containing copper is generally used, as the recovery of copper from the burnt pyrites forms an essential part of the Leblanc alkali industry (see p. 82). Coal pyrites produces tarry matter on burning, which is troublesome. A little pyrites is picked up on the beaches of the Isle of Sheppey, and pyrites from Wicklow in Ireland (40 per cent. S), Belgium (45 per cent. S), France (45 per cent. S), and Italy (49 per cent. S, with much arsenic), are used. Important deposits occur in Russia, Canada, and America. If in lumps, the pyrites is broken in a mill into pieces for the burners ; the fine powder requires special burners.

Brimstone.—Most of the sulphur used in Europe comes from Sicily. There are, however, deposits in New

Zealand, at Whale Island; in Texas, Chili, Russia, Japan, and Central Asia. The American deposits at Louisiana are very extensive (40,000,000 tons S), and are worked by the Frasch process, which consists in fusing the sulphur deposits *in situ* by superheated water under 6 atmospheres pressure passed down a tube; the melted sulphur is then forced up an internal aluminium tube by admitting compressed air through a concentric tube, on the emulsator principle (p. 25); on solidifying this is ready for use. In 1912 the Union Sulphur Co. made 280,000 tons of 99·5 per cent. purity (containing a trace of oil) by this process. Sulphur is used in acid manufacture when special purity, especially freedom from arsenic, is required; as in making invert sugar, or for electric batteries (cf. p. 264).

Zinc Blende.—Blende (20–30 per cent. S) furnishes sulphur dioxide as a by-product in roasting for zinc smelting. 65 per cent. of the Belgian acid was made in this way, and in America over 250,000 tons of acid were produced from blende in 1911. If roasted above 900°, no $ZnSO_4$ is formed:

$$2ZnS+3O_2=2ZnO+2SO_2$$

Gases from the smelting of lead and copper ores are now used to some extent. The roasting of silver, lead, and zinc concentrates from Broken Hill, New South Wales, provides a considerable amount of SO_2 available for the production of sulphuric acid.

Production of Sulphur Dioxide.—According to the source of sulphur, we have to consider:—

(1) Brimstone burners.

(2) Pyrites burners.

The burner gas contains 6 to 11 vol. per cent. excess O_2, and from 10 to 11 per cent. SO_2 if from brimstone, or 7 to 8 per cent. SO_2 if from pyrites; 5 per cent. of the total sulphur is usually present as SO_3. The advantages of using brimstone, beside the purity of the resulting acid, are the reduced chamber space (about two-thirds) required for the stronger gas, and the reduction of labour for the furnaces. Pyrites, however, costs only about half as much as brimstone, and the impurities then introduced into the acid do not usually matter. (Arsenic is often specially separated.)

Brimstone Burners.—Lunge's double furnace is largely used, the sulphur being placed on iron trays supported in a furnace. Cold air enters under the trays and regulates the temperature. The hot gases from the sulphur pass over the nitre pots (cf. below). Only 2 lbs. S are burnt per sq. ft. of surface per hour on the trays. Oddo (1910) proposed to burn briquettes formed of 1 part crude sulphur and 5 parts ore, giving 50 per cent. S, but this is still too expensive. In America Tromblee and Paull's rotary kilns are used for burning sulphur. They will burn 600 lbs. sulphur per day, and yield up to 18 per cent. SO_2 in the gas. Sulphur burning is somewhat difficult, as superheating, with distillation of sulphur, may occur.

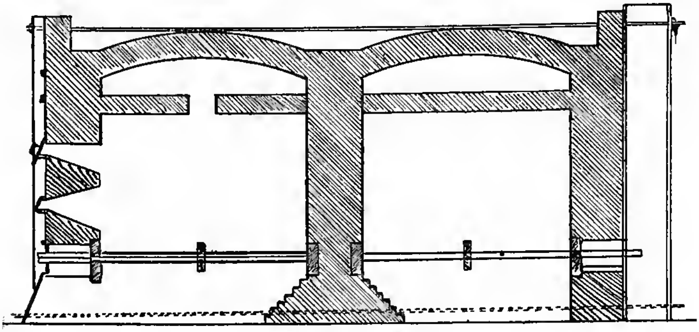


Fig. 2.—Pyrites Burner for Lumps.

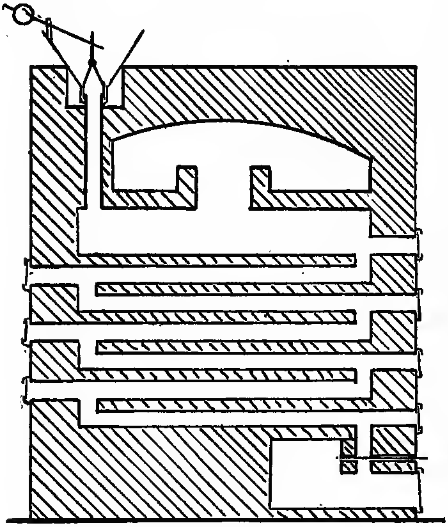


Fig. 3.—Pyrites Burner for Powder.

Pyrites Kilns or Burners.—These are designed for: (1) lumps, or (2) powder. Those for lumps are ordinary brickwork fireplaces with flues and bars (Fig. 2), on which the pyrites is placed, the kindling being effected by a little red-hot coke on the top, the temperature of the gas is 400°–500°. The air supply is regulated by sliding doors. For powder, Maletra, Delplace, or similar furnaces are used, consisting

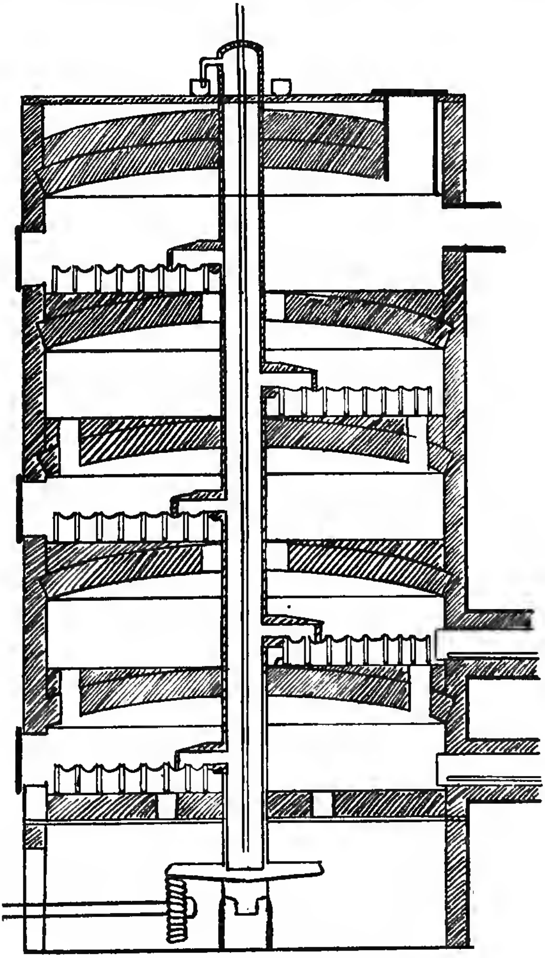


FIG. 4.—Herreshoff Pyrites Burner.

of a series of hearths over which powder is raked (Fig. 3); ignition is started by a separate hearth which is bricked up later, and finally the burnt pyrites falls into a cooling box. In the "grate furnaces" as used 10 cwt. are burned in 24 hours; in Maletra furnaces 13 cwt.; or 5 cwt. and 2 cwt. per sq. yd. per 24 hours respectively. The Delplace furnace is similar. Rotary furnaces (first introduced by Macdougall in 1870) are largely used, now of an upright type (Fig. 4) (Wedge furnace and Herreshoff furnace), with fixed body and trays and rotating scrapers, the shaft being hollow and cooled by water or air, and the scrapers having blades which push the material to the centre and circumference of the trays, alternately. Wedge furnaces will calcine 40 tons of pyrites per 24 hours. The burnt pyrites contains 0·75–3 per cent. S. It is now heated in revolving kilns with waste gas ("Nodulizing kiln") to remove most of the sulphur, and used in the blast furnace for production of iron.

The gases pass through dust chambers with baffles, or a broken brickwork mass, and then to the Glover tower. Inclined rotary furnaces are used in some Italian works.

Nitre.—After the pyrites burners come the arrangements for introducing the oxides of nitrogen. They are produced:

(i) From *nitre-pots* containing a mixture of sodium nitrate and sulphuric acid, placed in the flue from the pyrites burners to the Glover tower. This is the usual method in English works. About 3 parts of nitre are used for every 100 parts of sulphur burnt.

(ii) By spraying liquid nitric acid, or solution of sodium nitrate, into the lead chamber, or adding them to the Glover tower. This method is used in many Continental works.

(iii) By oxidizing ammonia mixed with air in a special apparatus, in which the mixture is passed over a heated catalyst, *e.g.* platinum.

For further information on the consumption of nitre, see pp. 34 and 238.

The Lead Chambers.—These are usually made from lead plates free from antimony, weighing 6–7 lbs. per sq. ft. (about ⅛ in. thick), the edges autogenously welded together and having lead straps also welded on for support on a wooden framework. The sides are suspended in a large flat dish made by turning up the edges of the sheet forming the bottom by 1–2½ ft. In British works the tops are often left exposed; on the Continent they are roofed in. In all cases the sides are protected by wood or corrugated iron walls. The chambers are rectangular in shape, 100–130 ft. long by 20–30 ft. wide by 16–25 ft. high. If water-spray is used instead of steam, they are narrower and higher. Chamber capacity up to 150,000 cu. ft. is often used. In England all the chambers are of the same size, three or four forming a set for one lot of kilns. In France one large, with smaller chambers before and after, is used; in Germany, frequently two large and two small. They are connected by pipes of 10–12 lbs. lead; there is some evidence that the gases should leave at the top and enter at the bottom. The size of chamber depends on that of the Glover and Gay Lussac towers; with average towers it is 16–20 cu. ft. per lb. S burned per 24 hours. Good chambers may last about 10 years, with occasional repair. The necessity for using such a large reaction space as the chambers follows from the consideration of the chemical reactions which take place in the formation of sulphuric acid. In Lunge's system of equations, all the reactions would, so far as we know, take place very rapidly except (4), in which the oxidation of NO is concerned. This reaction:

$$2NO+O_2=2NO_2$$

is fairly slow, especially when the NO is diluted with a large volume of air, and it would require an appreciable time of contact. Again, if the chamber space were unduly reduced, the formation of "chamber crystals" or solid nitrosulphonic acid might occur, which, if afterwards hydrolyzed in contact with the lead, would lead to corrosion of the latter owing to formation of nitric acid. If the acid in the chambers is too dilute (below 40 per cent.) nitrous oxide and even nitrogen are produced from the NO, and as these pass unchanged through the Gay Lussac tower, a loss of oxides of nitrogen results. This is, in fact, the case to a small extent even in correct working. Possibly these are derived from the decomposition of oxygen compounds of sulphur and nitrogen formed in the chambers :

$$N_2O_3+2SO_2+H_2O=2HSO_3NO$$
$$2NO.SO_3H+H_2O=2H_2SO_4+N_2O$$

Nitrososulphuric acid, HSO_3NO, is, however, a hypothetical substance.

Steam is admitted to the chambers from a boiler ; the use of steam has lately declined, Sprengel's *water-spray* system having been successfully used in England ; it has for some time been used in German works (*e.g.* Griesheim). The *draught* through the system is provided by a chimney, or leaded-iron fans, or blowers, usually placed between the last chamber and the Gay Lussac tower.

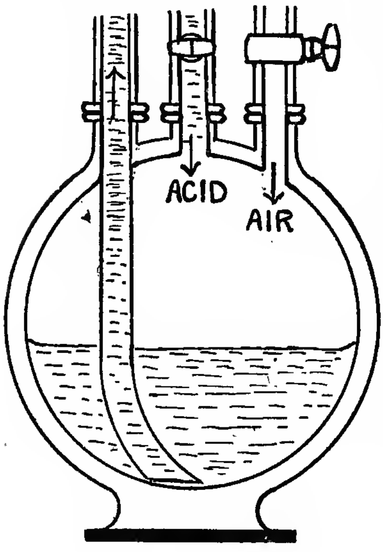


FIG. 5.—Acid Egg.

The *chamber acid* contains 60–70 per cent. H_2SO_4.

The Gay Lussac Tower.—This is made with lead walls of 8–10-lb. lead, with a "turned-up" lead bottom of 12–18-lb. lead, packed with coke, etc., and the lower part lined with blue bricks without mortar. It is built up in brickwork, is 4–10 ft. wide and 30–50 ft. high, its cubic content being at least 1 per cent. that of the chambers. The coke packing, although most used in England, tends to disintegrate, and cylinders, or balls, of acid-proof stoneware are coming into use. Acid is sprinkled over this packing by a kind of "Barker's Mill," or an intermittent siphon tank, being forced up to the top by an "acid-egg" (Fig. 5), an "emulsator" (Fig. 6), or by centrifugal multi-stage pumps. The acid should not be weaker than 144° Tw., and the temperature not higher than 30° C.:

$$N_2O_3 + 2H_2SO_4 = 2HNSO_5 + H_2O$$

The "Nitrous vitriol" formed contains 1–2 per cent. N_2O_3; if excess of SO_2 is used, a purple acid, H_2SNO_5, is formed.

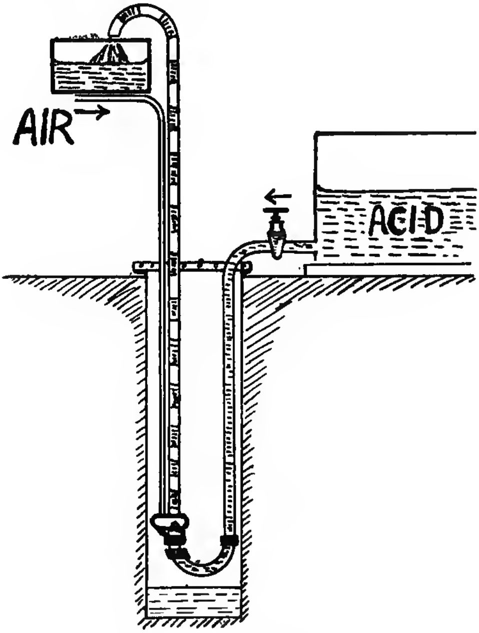


FIG. 6.—Emulsator.

In new plants, two or more Gay Lussac towers are usually erected.

The Glover Tower.—This (Fig. 7) is exposed to a higher temperature than the Gay Lussac tower, and is more strongly built of 14–18-lb. lead sides and 35-lb. lead bottom, and is lined with acid-resisting bricks or volvic-lava without mortar, 2 ft. 3 in. thick at the bottom, 18 in. above the grating, and 4½ in. at the top. The packing is usually flints or acid-proof blocks; or in America, quartz rock, and on the Continent, volvic-lava. Larger lumps are placed at the bottom of the tower. Lunge's special plate packing is also used. The height is 20–30 ft., but the volume is made equal to that of the Gay Lussac by increased section, *e.g.* 9–10 ft. square. The gases enter through a cast-iron pipe. There are two storage tanks on the top, one for nitrous vitriol, the other for chamber acid, and the two streams mix in a distributing box before passing down the tower. The hot concentrated acid (about 76 per cent.) leaves the " saucer " at the bottom by a lip, passing through silica, or lead, cooling coils. The temperature of the entering gases is 300°–400°; that of the exit gases is 50°–80°. If two towers are used, the first removes dust. Some acid is produced in the Glover tower, since the elimination of oxides of nitrogen occurs chiefly according to Lunge's third equation, *i.e.* reduction by SO_2; about ten times as much acid is produced as in an equal volume of chamber space.

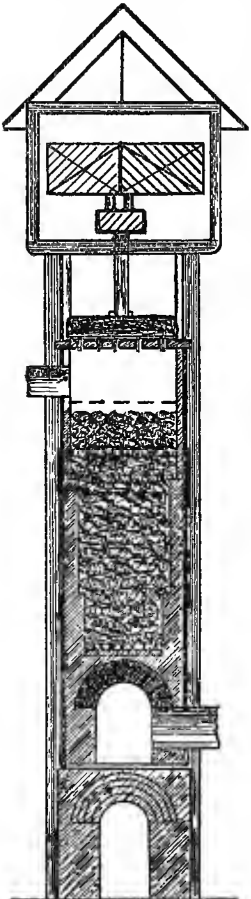


FIG. 7.—Glover Tower.

Method of Working a Chamber Plant.—The chambers are luted with 90°–100° Tw. acid at the start (not water), and excess nitre is used till the gases show a distinct colour with the pyrites kilns working. The Gay Lussac tower and steam are then started, and the nitre reduced to a minimum. The strength of the chamber acid is kept at 120°–125° Tw. (England), or 106°–110° Tw. (Continent). The chemical change is most rapid in the first half of the first chamber; it then slackens, but revives in the second (due to mixing in the pipes and cooling).

The exit gases are analyzed as they pass out of the Gay

Lussac tower, as well as the acid produced, which is collected from the chambers by "drip-pipes." (For analytical control see Lunge and Hurter, "Alkali Makers' Handbook," p. 98.) In successful working the following conditions are satisfied :—

	First chamber.	Second and intermediate chambers.	Last chamber.
Colour :	Colourless	Reddish-yellow ("pale" gases indicate shortage of nitre, O_2, or steam)	Dark red
Temperature :	80	60°	40°
Pressure :	slightly >atm.	—	slightly <atm.

The yield should be about 98 per cent. conversion of the sulphur burnt as pyrites.

Modern Chamber Systems.—(1) *Tangential Chambers.*

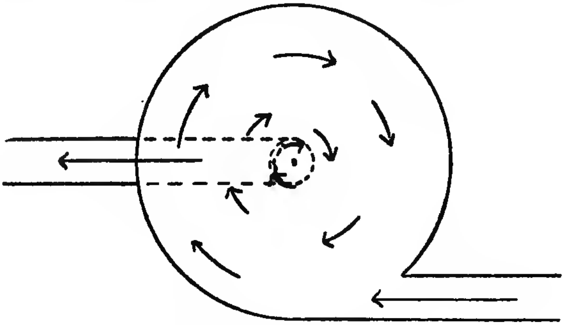


FIG. 8.—Tangential Chamber.

Th. Meyer in 1898 overcame the difficulty of mixing (and consequent excessive space required) in ordinary chambers, by using circular chambers (Fig. 8), and allowing the gases to enter tangentially so as to produce a spiral flow. Only two-thirds the space is then needed, and less lead is required for the same volume, on account of the shape. Five such towers in series may be used. In 1903, such chambers with a capacity of 360,000 cu. ft. had been erected, producing 160 tons H_2SO_4 per day ; each cu. ft. produced about 1½ lbs. H_2SO_4 per 24 hours. Circular chambers, with water cooling, have also been installed in some English works, without the spiral flow system (Mills-Packard system).

(2) *Falding's Single Chamber* (1909).—A New York patent in which a single chamber $1\frac{1}{2}$ times as high as broad, is used, and the gases cooled before entering the Gay Lussac tower. It has long been the practice in some European works to use tall chambers; 40 per cent. saving of lead is claimed. This system is said to be working satisfactorily in America.

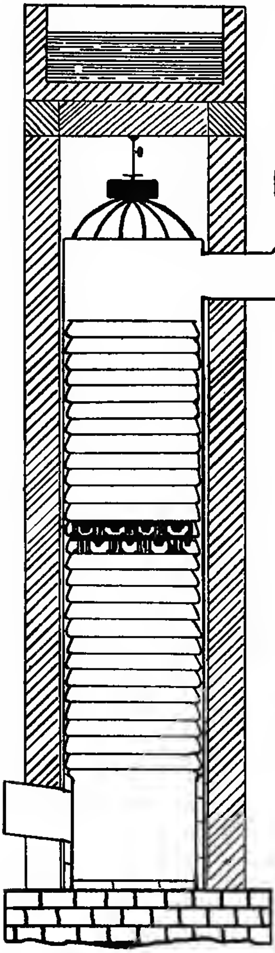


FIG. 9.—Plate Tower.

(3) *Lunge and Rohrmann Plate-Towers.*—In 1887 Lunge proposed to economize chamber space by the use of towers with perforated porcelain discs (Fig. 9). In 1893 the use of such towers had become extensive, in conjunction with chambers. 100 cu. ft. of tower space produces as much acid as 750 cu. ft. tangential, of 11,000 cu. ft. rectangular chamber space. They offer an increased resistance to the gas flow, requiring an aspirator at the end of the system, and their initial cost is much higher than for chambers for equal pioduction.

(4) *The Opl Tower system* is a series of six or eight such towers in series, without chambers. Such systems were successfully used at Griesheim in 1909, and are working satisfactorily in two English works. In the latter, six towers are used, the first three on

the Glover principle, and the last three as Gay Lussac towers. Water is added to the second, third, and fourth; fresh nitric acid to the second tower. All the acid passes through the first tower, and thence to coolers. The exit gases are scrubbed.

In tower systems the chemical reactions occur in the liquid passing through, not in the gas, as in chamber processes, hence the saving of space. The ordinary chamber space is from 10 to 19 cu. ft. per lb. S burnt per 24 hours; in the Opl tower system this is reduced to 2 cu. ft.

Reports of the working of the new chamber and tower systems are satisfactory; these improvements have doubtlessly strengthened the position of the chamber system, as opposed to the newer contact process, for the manufacture of sulphuric acid. In the liquid phase the reactions occurring are probably (4) and (3) of Lunge's scheme, alternately. According to Trautz, the formation and hydrolysis of nitrosulphonic acid in solution occur practically instantaneously.

Purification of Sulphuric Acid.—Arsenic is removed by treating the chamber acid with sulphuretted hydrogen (prepared from ferrous sulphide and dilute sulphuric acid) either in towers or in Davis's de-arsenicator plants, which consist of closed tanks with agitators. The precipitated As_2S_3 is filtered off through porous earthenware plates by suction or pressure; nitrogen oxides, antimony, lead, and presumably selenium, are simultaneously separated, and only a little iron is left in the acid as impurity. This iron may separate as ferric sulphate during subsequent concentration and give trouble. Another process is to add a little hydrochloric acid, and blow out the volatile $AsCl_3$ from the strong acid, or remove it by shaking with tar oils, when a kind of soap is produced.

Concentration of Sulphuric Acid.—The weak acid from the chambers, about 65 per cent. H_2SO_4, is concentrated in the Glover tower to 78 per cent., and acid of this strength may also be obtained by evaporating chamber acid in lead pans, the heating being effected either by hot gases passing over the surface, or by heating underneath, in which case the lead pans are protected by iron plates. With 3 pans, 6 ft. by 3 ft. by 1 ft., 3 tons of acid may be concentrated in 24 hours with half a ton of coal. Further concentration of the 78 per cent. acid is then carried out in various ways. Concentration of acid over 93 per cent. may be done in large cast-iron pots with lead rims. Up to 93–98 per cent. special apparatus is required.

The thermal efficiency of a concentrating plant may be determined on the following lines (cf. A. W. Porter, *Trans. Faraday Soc.*, 1917, for most recent data). The total heat required for concentration may be regarded as composed of three parts :—

(i) The heat required to raise the dilute acid from the temperature at which it is supplied to the temperature of concentration (Q_S) ;

(ii) The heat of dissociation into strong acid and free water, which is the same as the heat of dilution (Q_D) ;

(iii) The heat of evaporation of the water (Q_E).

If it is assumed that these are independent of temperature, a very rough approximation to the total heat may be obtained from the following table (C.H.U.=heat required to raise 1 lb. water 1° C.) :—

Concentration of acid.		Q_S.	Q_D.	Q_V.	Q total for mass containing 1 lb. H_2SO_4.
° Tw.	% H_2SO_4.				
168	96	103	—	2·12	105·12
155	84·5	104	64	95·5	263·5
130	73·1	107	95	196·0	398·0
111	64·5	108·5	113	291·0	512·5
101	60·0	116	124	349·0	589·0
84	52·2	138	133	488·0	759·0
61	40·0	193	153	795·0	1141·0
57	37·7	211	152·5	880·0	1243·5
29	20·0	440	173	2120·0	2733·0

Various types of concentrating apparatus have been in use at different times, many of which are now practically obsolete. Among the older forms may be mentioned—

(i) Glass retorts, in which the acid is boiled, either single retorts (Chance Bros., Oldbury), or retorts in cascades (Gridley).

(ii) Large glass beakers with lips, in cascade similar to the cascades now used (Webb, Levinstein).

(iii) Platinum, platinum-iridium, or gold pans, in the form of flat pans with corrugated bottom. Kessler used a platinum dish with a lead cover. These expensive plants are now going out of use, the metal being sold or used in the contact process as a catalytic material.

The methods largely used at present are of three types :—

(1) Kessler's Process.
(2) The Cascade Process.
(3) The Gaillard Tower.

Kessler's Process.—Hot gases pass over the surface of the acid contained in a shallow trough of volvic-lava, or acid-resisting stone, enclosed in a thick lead jacket (Fig. 10). Strong acid is left, and the fumes pass on to a tower formed in the lower part of lava and in the upper part of lead, where they give up sulphuric acid to descending weak acid, steam passing on. Kessler's apparatus gives very satisfactory results when only small quantities of acid are dealt with, and is used in several English works.

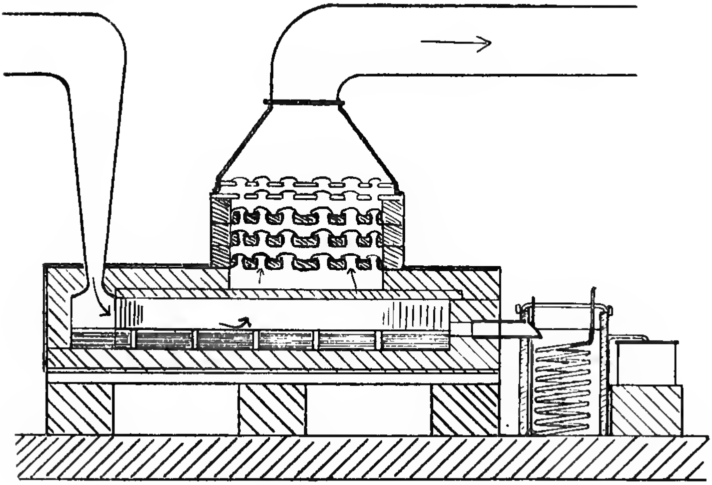


Fig. 10.—Kessler Concentrating Apparatus.

The Cascade Process.—The acid flows down a cascade (Fig. 11) of porcelain beakers, silica basins, or pans of acid-resisting metal. Porcelain beakers are attacked, and silica may develop fine cracks. Acid-resisting metals used are *ironac* (passive iron rich in silicon and poor in carbon, made by Haughtons' Metallic Packing Co.), *narki* (Varley & Co.), and *tantiron* (iron and 15 per cent. silicon made by the Lennox Foundry Co.).

The vesels are arranged on a kind of stairway, in pairs, the non-metallic kinds resting on asbestos rings in iron saucers, and are heated below by flues. The acid runs down, and hot air sweeps up over its surface. The hot concentrated acid from the last step goes through a lead cooler to a lead storage tank. Troublesome bumping is often caused by ferric sulphate separating out at a certain stage of the cascade.

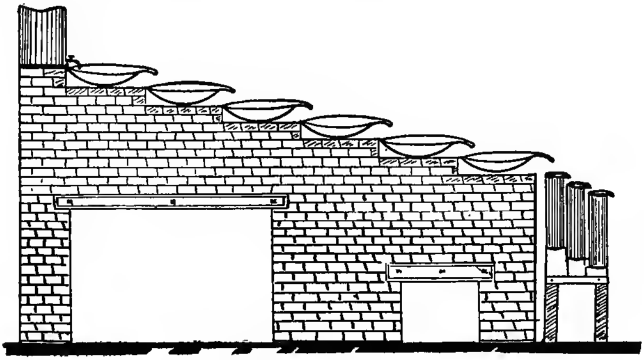


FIG. 11.—Cascade Concentrating Plant.

The Gaillard Tower (1906) is the most efficient method when large volumes of acid are dealt with, and is being introduced in large numbers. The acid is sprayed by three Körting jets down an empty slightly conical tower (Fig. 12) built of volvic-lava, or acid-resisting bricks set in a special manner with acid-resisting mortar, and hot gases from a coke furnace, freed from dust, and containing as little carbon monoxide as possible, pass up the tower. The fine mist of acid falls down on to a baffle of acid-resisting stone, and the liquid then drops into the lower part of the tower, which is luted with lead. This concentrated acid runs out into a lead settling tank, in which mud settles out. The acid then runs out through a pipe into a lead tank in which is a lead cooling spiral. The gases passing out of the tower pass through a recuperator, which is a smaller empty lead tower, down which a spray of weak acid is passed. About half the acid to be concentrated is passed down the recuperator. The final gases are scrubbed in lead boxes filled with wet coke, or passed through a Cottrell electrostatic precipitator, in which the acid mist condenses to liquid.

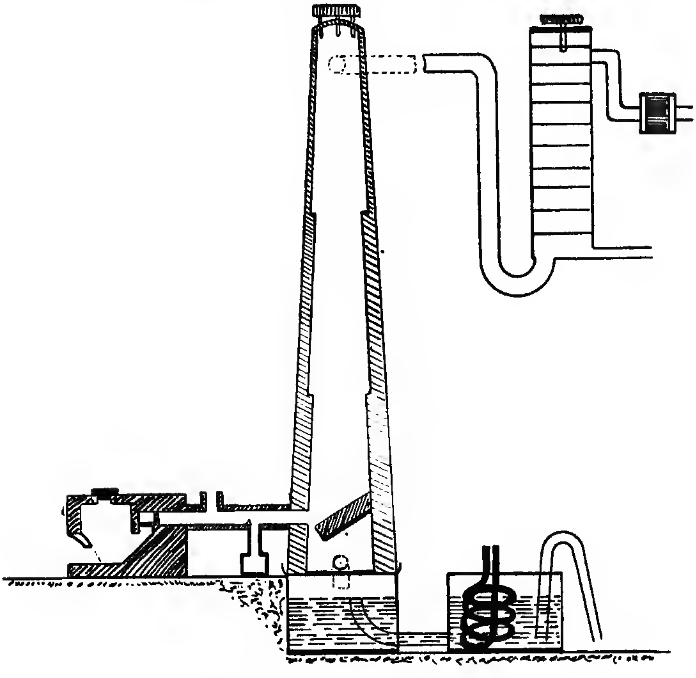


FIG. 12.—The Gaillard Tower.

The gases enter the main tower at 900°–1050°; those leaving the recuperator are at 200°. Secondary air is admitted in the flue passing from the furnace to produce the maximum amount of CO_2; the gases entering the tower contain 12–15 per cent. CO_2. 24 cwt. coke are used in a charge with the furnace working discontinuously; with producer gas firing continuous working is obtained. A tower 60 ft. high and 6 ft. diameter produces 40 tons 95–96 per cent. acid per day, with a loss of 3–5 per cent. due to leakage, and loss of SO_2 and SO_3 in the exit gases. The exit gases from any concentrating system must not in England contain more than 1½ grains SO_3 per cu. ft. The losses in cascade systems may amount to 15–20 per cent. The consumption of fuel in the tower is about 1½ to 2 cwts. coke per ton of 96 per cent. acid produced.

Losses in the Chamber Process.—100 parts of sulphur burnt in the kilns as brimstone or pyrites should yield 306¼ parts of H_2SO_4, but in practice the yield is less, owing to loss from the following sources:—

(1) Incomplete removal of sulphur from the pyrites, or sublimation of sulphur.
(2) Leakage in working the burners, or from the chambers, towers, etc.
(3) Escape of SO_2, or uncondensed H_2SO_4, in the exit gases.

The actual yield is usually 278–285 parts H_2SO_4 per 100 S burnt as pyrites, and 290–300 when burnt as brimstone.

The consumption of nitre varies for the different systems; it has been estimated as follows, per 100 parts of sulphur burnt:—

(1) Ordinary chamber process without Gay Lussac towers: 10 parts.
(2) Ordinary chamber process with Gay Lussac towers: 2·5–4 parts.
(3) Meyer's tangential chambers: 2·7 parts; with intermediate towers, fans, and water-spray instead of steam: 1·8 parts.
(4) Niedenführ system with plate-towers: 2·2–2·45 parts.
(5) Falding's chamber: 1–1·5 parts.
(6) Opl tower system: 2·25 parts.

The Law of Mass Action and Applications of Thermodynamics.—According to the earlier ideas of chemical affinity, a chemical reaction was the result of the play of the affinities of the various elements, or groups, in the reacting substances. Thus, the reaction—

$$NaCl+H_2SO_4=NaHSO_4+HCl$$

proceeds because the affinities of Na and HSO_4 and of H and Cl are greater than those of Na and Cl and of H and HSO_4, respectively. It follows at once that if a chemical reaction commences, it should go on to the end, because so long as the affinities can act, there is no reason why they should not do so. Speaking generally, if we consider the simple case—

$$AB+C=AC+B$$

if the affinity of C for A is greater than the affinity of B for A, then C will displace B completely from the compound AB. This is Bergman's theory of affinity ("Essay on Elective Attractions," 1775).

It was found, however, particularly in the researches of Berthollet ("Chemical Statics," 1803), that most chemical reactions do not go to completion. Thus, in the caustification of mild alkali by lime, the reaction—

$$(1)\ K_2CO_3+Ca(OH)_2=2KOH+CaCO_3$$

is not quantitative ; some carbonate is always left. Further, if calcium carbonate is boiled with caustic alkali, some mild alkali is formed :

$$(2)\ 2KOH+CaCO_3=K_2CO_3+Ca(OH)_2$$

Reactions are therefore generally *incomplete*, and *reversible*. This result alone is sufficient to disprove Bergman's theory, but Berthollet made a further discovery of fundamental importance. He found that the extent of decomposition depended on the quantity of the reacting substance, present in a given volume, which was available for reaction—a factor which he called the *active mass*. Thus, if we pour off the solution containing KOH and K_2CO_3 in reaction (2), when it has ceased to react any further, or, as Berthollet said, when it is in *chemical equilibrium* with the solids, and replace it by a fresh solution of KOH, then further decomposition occurs, and by repeating the process the $CaCO_3$ may be completely converted into $Ca(OH)_2$. Berthollet therefore clearly realized that the mass of a reacting substance has an important effect on the course of the reaction, but unfortunately he did not know how to specify the "active mass" so as to lead to quantitative conclusions. This was reserved for Guldberg and Waage (1867), who succeeded in expressing Berthollet's conceptions in a mathematical form. The resulting Law of Mass Action is undoubtedly the basis of all modern chemical industry on its scientific side. Thus, if a certain product is to be made by a chemical process, the first thing which would be done is to write down the stoichiometric equation, showing the course of the reaction. Thus, if it is desired to prepare ammonia from its elements, we have the equation—

$$N_2+3H_2=2NH_3$$

This, however, does not give us the slightest information on the most important points, first of all whether the reaction is possible at all, and secondly, if it is, what will be the yield. Without some guidance we should consider the yield as quite fortuitous, or at best the result of following empirical rules—as is still largely the case in Organic Chemistry. By means of the law of mass action we can foresee the whole possibilities of a reaction, provided we have made one or two equilibrium measurements at different temperatures. This will be explained further on; a short account of the law of mass action will first be given.

Guldberg and Waage showed that a suitable specification of the active mass is the *concentration* of a component, this being the number of molecular weights per unit volume; *e.g.* the number of gram-molecules per litre, or shortly, the number of *mols* per litre.

If we denote the equilibrium state, when no further chemical change takes place, by the equation—

$$AB+C\rightleftarrows AC+B$$

to take a simple case, then it is found that in this state all the reacting substances, AB, C, AC, and B, are present in finite amounts. Some of these amounts may be very small; thus in the reaction—

$$BaCl_2+H_2SO_4 \rightleftarrows BaSO_4+HCl$$

in aqueous solution, traces of $BaCl_2$ and H_2SO_4 are always present. Guldberg and Waage further pointed out that this equilibrium state is attained, not by the absence of any chemical change at all, but by the simultaneous occurrence of the forward and reverse reactions—

$$AB+C \rightarrow AC+B$$
$$AC+B \rightarrow AB+C$$

so that as much of any one substance, say AC, is formed in a given instant by the direct reaction as is used up again by the reverse reaction. Hence the use of the symbol "$\rightleftarrows$" This conception has been verified by experiment; to take a well-known case, the rates of formation and decomposition of hydrogen iodide approach equality as equilibrium is reached—

$$I_2+H_2 \rightleftarrows 2HI$$

If we denote the concentrations of the four substances present by [AB], [C], [AC], [B], then the law of mass action states that when equilibrium is attained the following equation holds good:—

$$[AB][C]=[AC][B]\times\text{Constant}$$

or

$$\frac{[AC][B]}{[AB][C]}=\text{Constant}$$

Generally, if we have the reaction—

$$n_1A_1+n_2A_2+n_3A_3+\ \ldots\ =n_1'A_1'+n_2'A_2'+n_3'A_3'+\ \ldots$$

in which n_1 molecules of A_1 react with n_2 molecules of A_2, and so on, to produce n_1' molecules of A_1', and so on, the law of mass action may be expressed in the form—

$$\frac{[A_1']^{n_1'}[A_2']^{n_2'}[A_3']^{n_3'}\ \ldots}{[A_1]^{n_1}[A_2]^{n_2}[A_3]^{n_3}\ \ldots}=\text{Constant}=K$$

More conveniently we can write—

$$\Sigma n_1 \log [A_1]=\log K$$

The law of mass action may be deduced theoretically, either on kinetic grounds, or from the principles of thermodynamics (see, for example Partington, "Thermodynamics," pp. 322 *et seq.*). It must be emphasized that it only disentangles one of the factors which influence the course of a chemical reaction, viz. the effect of the varying concentrations of the interacting substances. Among the other factors are: the chemical affinities, the temperature, and pressure. Thus K is a constant:—

(i) with given interacting substances; *i.e.* affinities;
(ii) at a fixed temperature;
(iii) at a fixed pressure.

K is therefore usually a function of all these variables. It is, however, usually called the Equilibrium Constant.

The law of mass action alone is therefore not sufficient to give us complete information as to the course of a reaction, or the *yield*, under practical conditions, because it only applies, with a constant value of K, to a particular temperature. In order to complete our information we must know how K varies with the temperature. This is a problem which can be solved by a simple application of the principles of thermodynamics, and its solution forms one of the most useful applications of that science. Thermodynamics is at least as useful in applied chemistry as it is in engineering, and is rapidly becoming the foundation of modern industrial chemistry. Previously, and even in some cases to-day, an incorrect theory was in vogue, namely, the so-called Principle of Maximum Work of the thermochemists, M. Berthelot and J. Thomsen. Stated briefly, this was as follows. If the reaction—

$$AB+C=AC+B$$

is attended by an evolution of heat, then it will occur in practice. In other words, if Q denotes the heat of formation of AB, and Q′ that of AC, then C will displace B from the compound AB provided that $Q'>Q$.

In place of this incorrect criterion, which is disproved by every endothermic reaction, we may use the principles of thermodynamics, in particular the Second Law. It can be shown, in fact, that a process can only occur spontaneously when, if suitably conducted, it is capable of furnishing useful work. By "useful work" is meant energy in such a form that it can be directly and completely converted into the potential energy of a raised weight, without any other energy changes occurring anywhere. In other words, a spontaneous process involves the loss by the system undergoing the process of a store of energy which is convertible under proper conditions completely into useful work. Such energy is called Available Energy, or Free Energy. Thus, if a piece of zinc is placed in a solution of copper sulphate, it passes into solution, and throws out copper, because the reaction—

$$Zn+CuSO_4 \rightarrow Cu+ZnSO_4$$

if carried out in a Daniell's cell can produce an electric current, which is directly convertible into useful work by means of an electromotor. When the reaction occurs spontaneously, however, the available energy is not recovered as work, but in the only partially available state of heat.

The Second Law of Thermodynamics may be stated in the following form :—

The maximum work obtainable in an isothermal process is equal to the diminution of available energy, and is independent of the way in which the process is performed, provided it occurs isothermally and reversibly.

It is possible to calculate the maximum work, or diminution of available energy, which we shall denote by A, in many cases. In particular, when the system is composed of gases or dilute solutions, it is given by the expression—

$$A=RT\log_e K-RT\Sigma n_1 \log_e [A_1]$$

where the external work due to change of volume, $\Sigma n_1 RT$, is neglected (cf. "Thermodynamics," par. 144) ;

R is the general gas constant : $8{\cdot}315 \times 10^7$ erg/degrees C. in absolute units ;

T is the absolute temperature ;

K is the equilibrium constant, as defined above ;

$[A_1]$ is the initial concentration of the first reacting substance, and n_1 the number of molecules of it which enter into reaction.

Terms referring to the products of reaction are taken as positive, and heat Q evolved during the reaction is taken as positive.

Thus, in the reaction $2H_2+O_2 \rightarrow 2H_2O$—

$$K=[H_2O]^2/[H_2]^2[O_2]$$

and Q is the heat of formation of water.

In equilibrium no reaction occurs, hence—

$$A=0$$

from which follows the law of mass action—

$$\log_e K=\Sigma n_1 \log_e [A_1 e]$$

where $[A_1 e]$ is the concentration of A_1 in equilibrium.

It is a consequence of the First Law of Thermodynamics that the heat of reaction at constant volume, Q_v, is a function of temperature of the form—

$$Q_v=Q_0+\Sigma\int n_1 c_1 dT \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Q_0 is the heat of reaction at absolute zero;

$\Sigma n_1 c_1$ is the algebraic sum of the molecular heat capacities of the reacting substances, products of reaction being again taken as positive.

Thus, in the reaction just considered—

$$\Sigma n_1 c_1=2C_{vH_2O}-(2C_{vH_2}+C_{vO_2})$$

where C_v is the molecular heat at constant volume, itself a function of temperature.

An application of the Second Law of Thermodynamics leads to the equation—

$$\frac{d \log_e K}{dT}=\frac{-Q_v}{RT^2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

("Thermodynamics," par. 147). Q_v is positive for heat evolved.

If we substitute for Q_v its value given by formula (2), we have—

$$\frac{d \log_e K}{dT}=-\frac{Q_0+\Sigma\int n_1 c_1 dT}{RT^2} \quad . \quad . \quad . \quad (3)$$

which contains the whole theory of the influence of temperature on equilibrium. This equation may be integrated when c_1 is known as a function of T. In the integration an arbitrary constant will enter, which cannot be evaluated from the purely thermal data Q and the values of c. Hence the value of K at one temperature must be known before we can make use of the equation. According to a new theorem introduced by Nernst (1906), the value of the integration constant can be obtained as a sum of terms depending only on the properties of the pure components, which may be determined once for all, and are then available for various calculations. If I is the integration constant

$$I = \Sigma n_1 i_1$$

where i_1 is called the Chemical Constant of the first component. Tables of these constants have been calculated, and an approximation to the equilibrium conditions can be made by using them, without making a single determination. This method has already found an application in technical chemistry ("Thermodynamics," par. 212).

Theory of the Contact Process.—In the reaction of the so-called Contact Process for the manufacture of sulphuric acid, which is considered in the next paragraph, we have—

$$2SO_2 + O_2 \rightleftarrows 2SO_3$$

In the equation of mass action—

$$\Sigma n_1 \log [A_1] = \log K$$

we shall have—

$$n_1 = -2\,;\ n_2 = -1\,;\ n_1' = 2$$

hence $$-2 \log [SO_2] - \log [O_2] + 2 \log [SO_3] = \log K$$

or $$\frac{[SO_3]^2}{[SO_2]^2[O_2]} = K$$

It is evident that, other things being equal, the yield of SO_3 is increased in the equilibrium state when either the concentration of the SO_2 or the concentration of the O_2 is increased, but an increase in the concentration of the SO_2 will have a more marked effect because the latter enters the product as a square. In actual practice, however, the aim is to get the maximum yield of SO_3 from a given amount of SO_2, hence it is necessary to use excess of oxygen, as otherwise unchanged SO_2 would pass over with the SO_3.

The equation—

$$\frac{[SO_3]}{[SO_2]}=\sqrt{K[O_2]}$$

shows that the ratio of SO_3 to SO_2 is proportional to the square root of the oxygen concentration.

If we use partial pressures instead of concentrations it is easy to show that—

$$p_1=[A_1]RT\,;$$

hence $$p_{so_3}/p_{so_2}=K'\sqrt{p_{o_2}}$$

where K′ is constant at a given temperature.

The following table gives the values of K′, *i.e.* of $p_{so_3}/p_{so_2}\cdot\sqrt{p_{o_3}}$, for different temperatures :—

t °C.	T abs.	K′ cal.	K′ obs.	Observer.
450	723	191·4	187·67	Knietsch.
500	773	70·0	72·3	,,
515	788	53·21	65·4	Bodländer
553	826	27·48	24·1	,,
600	873	13·30	14·9	Knietsch.
610	883	11·48	10·5	Bodländer.
700	973	3·55	4·84	Knietsch.
800	1073	1·21	1·81	,,
900	1173	0·20	0·57	,,

These results are shown in the curve in Fig. 13.

The effect of temperature on the value of K is to diminish the latter with rise of temperature, a result which follows from the equation—

$$\frac{d\log_e K}{dT}=\frac{-Q_V}{RT^2}$$

According to Berthelot the heat of reaction for

$$2SO_2+O_2\rightarrow 2SO_3$$

is 45,000 calories at room-temperature ; hence $Q_v=45{,}000$, and $\frac{d\log_e K}{dT}$ is negative.

To integrate the equation $\frac{d \log_e K}{dT} = \frac{-Q_v}{RT^2}$ we should have to know the specific heats of SO_2, O_2, and SO_3 at all the temperatures at which the equation is to be applied. In the case of SO_3, such data are not available. If we assume, roughly, that Q_v is constant, we have—

$$\log_e K = \frac{Q_v}{RT} + \text{constant} \quad . \quad . \quad . \quad . \quad (1)$$

Q_v will be, taking Berthelot's figure, 22,500 at the ordinary temperature; at higher temperatures it will diminish, and if we take 22,270 cal. as the mean value, the equation—

$$R \log_e K' = \frac{22{,}270}{T} - 20{\cdot}4 \quad . \quad . \quad . \quad (2)$$

is found to give values of K′ agreeing with experiment. R in *gram calories ÷ degrees C.* will be 1·985, and to convert common logarithms to natural logarithms we multiply by 2·3026, hence—

$$\log K' \times 2{\cdot}3026 \times 1{\cdot}985 = \frac{22{,}270}{T} - 20{\cdot}4$$

or

$$\log K' = \frac{4875}{T} - 4{\cdot}46 \quad . \quad . \quad . \quad . \quad (3)$$

The values of K′ from this equation are shown as crosses, the observed values as circles, in Fig. 13. The agreement is good.

The constant 20·4 in equation (2) was found by taking an experimentally found value of K′ at a given value of T and substituting in the equation. If we use Nernst's theorem we have to take the chemical constants of SO_2, O_2, and SO_3. The latter value is not known, but by assuming a probable value, an equation is obtained which agrees fairly well with the experimental results.

The *yield*—

$$x = \frac{SO_3}{SO_2 + SO_3}$$

may be calculated from the equation—

$$xSO_2 + xSO_3 = SO_3$$
$$\therefore (1 - x)SO_3 = xSO_2$$

$$\therefore \frac{SO_3}{SO_2} = \frac{x}{1-x}$$

and

$$\frac{x}{(1-x)\sqrt{p}} = K'$$

or

$$x = \frac{K'\sqrt{p_{O_3}}}{1+K'\sqrt{p_{O_2}}}$$

from which the yields at various temperatures and initial compositions may be calculated.

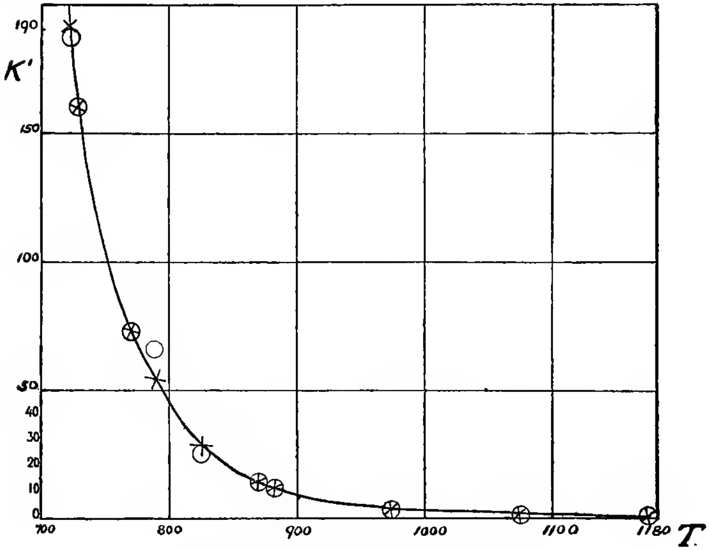


FIG. 13.—The SO_3—SO_2 Equilibrium.

If *a*, *b*, *c* are the percentages of SO_2, O_2, and N_2 in the initial mixture, prepared by burning pyrites in air, then since 0·5*ax* of the *b* volumes of O_2 are used up, and the volume is kept constant—

$$p_{O_2} = \frac{b - \frac{1}{2}ax}{100 - \frac{1}{2}ax} = \pi$$

and

$$x = \frac{K'}{K' + \sqrt{\frac{1}{\sqrt{\pi}}}}$$

From this equation Haber calculated the following table, which is directly applicable to the contact process operations in the works :—

Composition of initial gas—

$a = 7{\cdot}0$ per cent. SO_2
$b = 10{\cdot}4$ „ O_2
$c = 82{\cdot}6$ „ N_2

Temperature ° Centigrade.	K′.	Maximum equilibrium yield SO_3 x per cent.
434	181	97
550	20·4	85
645	5·14	60

The yield increases with fall of temperature, and it would at first appear as if the best working condition would be the lowest possible temperature. Another consideration, however, now enters the calculations.

If SO_2 and O_2 are mixed together at room temperature no appreciable reaction occurs, because the velocity of oxidation of SO_2 to SO_3, is very small under such conditions. In the presence of a catalyst, such as platinum, this velocity is increased, but even then it does not become sufficiently rapid for manufacturing processes until the temperature is about 400°. There are two conflicting conditions: the equilibrium yield (which is of course unaffected by the catalyst) is increased by lowering the temperature, but the velocity of reaction, or the yield per unit time, is increased by raising the temperature. There will, therefore, be an optimum temperature at which the best working yield will be obtained, and this will be arrived at by a consideration of the equilibrium and velocity curves. The velocity curves have to be determined by experiment, as there is no equation known which expresses the velocity of reaction as a function of temperature in the same way as that giving the variation of the equilibrium constant. The optimum temperature has been found to be 400°–450°, and it is very essential to maintain this temperature constant during the process, otherwise the yield falls off considerably.

Knietsch's curves for various conditions are shown in Figs. 14 and 15. Fig. 14 shows the percentage of SO_3 in the mixture at different temperatures, each curve corresponding with a different flow rate. By increasing the flow rate the temperature for maximum conversion increases, but the yield

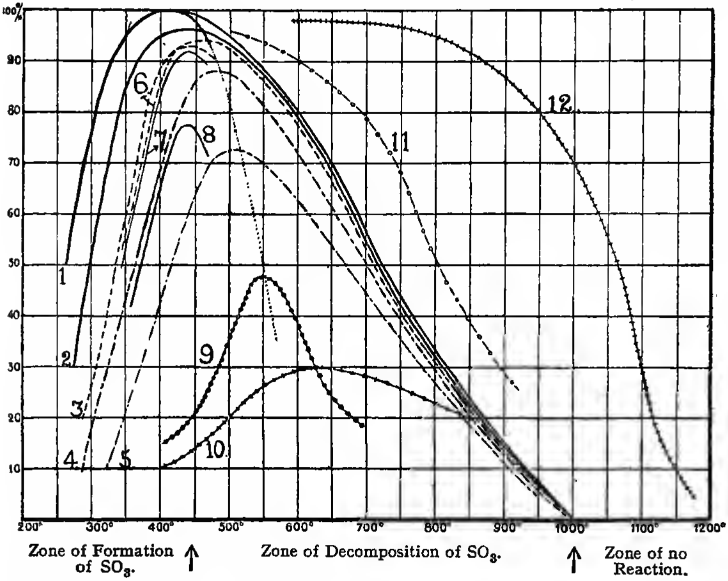


FIG. 14.—Isochronous Reaction, $2SO_2+3O_2=2SO_3+2O_2+22{,}600$ cal.

1, 2, 3, 4, 5. Technical burner gas containing 7 % SO_2, 10 % O, 83 % N. Platinized asbestos in porcelain tube as contact substance; rate of flow being 300, 1000, 2500, 7500, and 20,000 c.c. per minute respectively.

6. Platinum contact, pure stoichiometrical mixture. Rate of flow 7500 c.c. per minute.

7. Platinum contact at 500 c.c. per minute
8. ,, ,, 1000 ,, ,,

Stoichiometrical burner gas containing—
20 vol. % SO_2
10 ,, O
70 ,, N

9. Technical burner gas. Pyrites cinders ($Fe_2O_3.CuO$) as contact substance, and 500 c.c. per minute.

10. Technical burner gas through porcelain tube—bits of porcelain as contact substance. Rate=500 c.c. per minute.

11. SO_3 through tube filled with bits of porcelain and 500 c.c. per minute.

12. SO_3 through empty tube and 500 c.c. per minute.

diminishes, because although the velocity of conversion is increased, the percentage of SO_3 in equilibrium diminishes.

In Fig. 14, curve 1, it is seen that the reaction begins appreciably at 200°, and reaches completion at 420°, after which it falls off, and is negligible at 1000°. Increasing flow-rates shown by curves 1–6 in succession, cause maxima at higher temperatures, when more and more gas has to be dealt with by the catalyst as the flow-rate increases, and correspondingly higher temperatures and therefore reaction velocities were required, but the yield is smaller on account of the lowering of the equilibrium constant K′ with rise of temperature.

The curves in Fig. 15 show the influence of time of contact, or, what comes to the same thing, the quantity of platinum catalyst, on the yield. The best temperature is seen to be 450°.

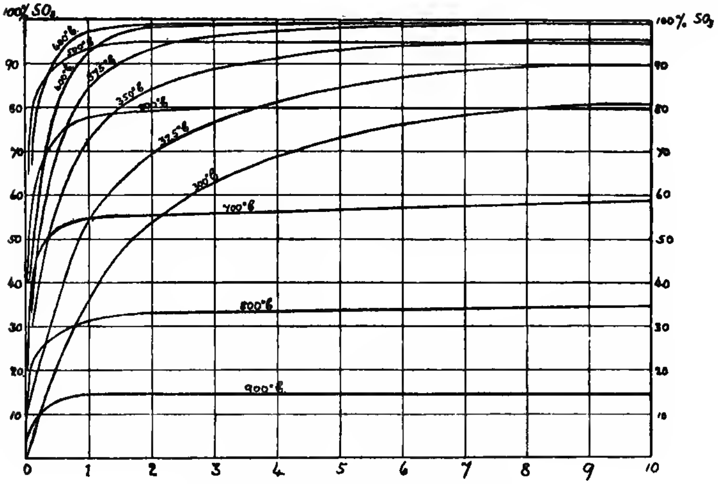


FIG. 15.—Contact Process for SO_3.

Some experiments on the kinetics of the contact process have been made, which seem to indicate that the reaction does not occur in the gas phase according to the equation for a termolecular reaction, but in a heterogeneous system, viz. on the surface of the platinum, and the velocity is largely dependent on the rates at which the gases reach the catalytic surface by diffusion.

Sulphuric Acid from Sulphates.—Reference has already been made to the old process of making sulphuric acid by distilling iron sulphate, formerly carried on in Bohemia. The reaction may be formulated either as—

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$

or

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$$

according to whether ferrous or ferric sulphate is distilled. In practice weathered pyrites was used, the product being dehydrated previous to distillation, so that probably $Fe_2(SO_4)_3$ was the chief constituent. According to Bodenstein and Tatsugi Susuki (1910), the first products are SO_2 and O_2, which then react in presence of the Fe_2O_3 acting as a catalyst, to produce SO_3—

$$2Fe_2(SO_4)_3 \rightleftarrows 2Fe_2O_3 + 6SO_2 + 3O_2$$
$$6SO_2 + 3O_2 \rightleftarrows 6SO_3.$$

In the gaseous phase we have—

$$K' = \frac{p_{so_3}{}^2}{p_{so_3}{}^2 p_{o_2}}$$

and in the heterogeneous equilibrium—

$$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3$$

we have from the Phase Rule a definite equilibrium pressure of SO_3 at a fixed temperature, because there are three phases (solid sulphate, solid oxide, gas) and two components (Fe_2O_3 and SO_3), hence only one degree of freedom.

Let P_{so_3} be the equilibrium pressure of SO_3 over the heated solid, then there is equilibrium when—

$$P_{so_3} = p_{so_2} = \sqrt{K' p_{o_2}} \times p_{so_2}$$

If $P_{so_3} > p_{so_2}\sqrt{K' . p_{o_2}}$, then the sulphate will be decomposed with formation of SO_3, SO_2, and O_2.

Another process which has been used on a large scale is that of heating gypsum, or calcium sulphate, with sand (Cummings, 1886)—

$$CaSO_4 + SiO_2 = CaSiO_3 + SO_3$$

If gypsum and sand are made into a paste with a little water, and heated in an autoclave to 600°–800° for several hours, H_2SO_4 is formed.

According to Cantilena (1914), finely powdered burnt gypsum and dried clay are mixed so that the ratio—

$$(SiO_2+Al_2O_3+Fe_2O_3) \text{ to } CaO$$

is from 0·43 to 0·5. The mixture is moulded with water into small bricks, which rapidly set, and these are heated in a furnace to 1600° in a plentiful stream of air and out of contact with fuel. The following reactions occur :—

At 1000° : $CaSO_4+SiO_2=CaSiO_3+SO_3$
At 1450° : $CaSO_4=CaO+SO_3$
At 1600° : $3CaO+2CaSiO_3=Ca_5Si_2O_9$

The residue is a kind of Portland cement. The gases leave the furnace at 500° and are used to dehydrate the gypsum at 155° before passing on to the sulphuric acid apparatus. If the air is enriched with oxygen, dissociation of SO_3 is diminished.

It is alleged that the production of sulphuric acid from gypsum has been used in Germany recently on a large scale, owing to the shortage of pyrites resulting from the blockade.

The Contact Process for the Manufacture of Sulphuric Acid.—P. Phillips of Bristol proposed in 1831 to produce sulphuric acid according to his own discovery, by passing a mixture of sulphur dioxide and oxygen over heated platinum sponge, whereby sulphur trioxide was formed, and absorbing the latter in water—

$$2SO_2+O_2=2SO_3$$
$$SO_3+H_2O=H_2SO_4$$

His process failed, as the platinum was rapidly "poisoned" by impurities in the SO_2, and became inactive.

Squire and Messel (1875), using pure gases obtained by Deville's process, *i.e.* dropping strong sulphuric acid on white-hot bricks and drying the gas over strong sulphuric acid, made fuming sulphuric acid, $H_2S_2O_7$, using platinized pumice as catalyst—

$$2H_2SO_4=2H_2O+2SO_2+O_2$$
$$2SO_2+O_2=2SO_3$$
$$SO_3+H_2SO_4=H_2S_2O_7$$

Later on, Squire used sulphur dioxide from sulphur, purified by dissolving in water under 4 atm. pressure and then expelling by steam, and this process was used in the works of the Thann Chemical Co., Alsace (1881).

Various other minor improvements were made in the interval between 1875 and 1898 by several firms, and several patents were taken out. Following the advice of C. Winckler, however, most manufacturers used the mixture of SO_2 and O_2 in the exact proportions of 2 : 1, in spite of the fact that excess of oxygen was beneficial according to the law of mass-action, enunciated as early as 1867. The first impetus to large-scale working came in 1898, when as a result of researches carried out in their laboratories by Dr. Knietsch, and by Drs. Krauss and von Berneck, respectively, the Badische Anilin und Soda Fabrik, of Ludwigshaven, and Meister Lucius und Brüning, of Höchst, simultaneously took out patents for the use of pyrites gases.

As a result of this work the important fact came to light that the poisoning of the platinum by pyrites gases was due to dust and impurities, especially arsenic, contained in them, and that if the gases are carefully scrubbed and purified before passing to the catalyst, the latter retains its activity unimpaired.

The equilibrium $2SO_2+O_2 \rightleftarrows 2SO_3$ is maintained at 450° with 94 per cent. of sulphur trioxide; if air is used instead of oxygen so that the proportions of SO_2 and O_2 are the same as before, the yield is 91 per cent., the diminution being caused by the dilution with nitrogen. The best result is obtained when the oxygen is present in three times the theoretical amount, viz. $2SO_3+3O_2$, which is almost exactly the composition of the gases from the pyrites burners. With these gases and a temperature of 400°–450° a yield of 98 per cent. is obtained (Knietsch). A large amount of heat is evolved in the reaction (cf. p. 43), and the catalytic mass has to be cooled by using a mixture of cold and preheated gases, as described below.

As catalysts the following materials have been proposed:—

(1) Platinum, in different forms (10 per cent. platinized

asbestos, platinized ferric oxide, and in the Grillo process platinized magnesium sulphate).

(2) Oxides and sulphates of iron, chromium, nickel, cobalt, manganese, uranium, vanadium, copper.

(3) Oxygen compounds of aluminium, beryllium, zirconium, cerium, and didymium.

(4) Mixtures of (1) with (2) and (3).

(5) Mixtures of (2) and (3).

(2), (3), and (5) are used only at high temperatures (above 600°).

The catalytic action of the platinum metals probably depends on intermediate oxide formation—

$$2Pt+O_2 \rightarrow 2PtO\ ;\ PtO+SO_2 \rightarrow Pt+SO_3$$

that of the oxides on the formation of sulphate—

$$2Fe_2O_3+6SO_2+3O_2 \rightarrow 2Fe_2(SO_4)_3 \rightarrow 2Fe_2O_3+6SO_3$$

The following is a brief description of the *Badische process*:—

The gases from the pyrites burners are first treated with a steam jet in a dust flue, and are then cooled to 100° C. in a tubular lead cooler, after which they are scrubbed with water to free them from all traces of mist, and dried with concentrated sulphuric acid. They should then show no fog in a beam of light. The cooled purified gases are forced through the contact apparatus (Fig. 16), which in the Badische process consists of a number of vertical iron pipes containing 10 per cent. platinized asbestos as a catalytic material, the whole being enclosed in an outer iron jacket. Part of the gas enters this outer jacket near the bottom, and passes upwards over the outside of the catalyst tubes, from which it takes heat; this heated gas then mixes with cold gas entering at the top, and by regulating the proportions of gas admitted above and below, the pre-heating is sufficient to cause the reaction to take place when the gases pass down through the catalyst tubes. Portions of gas may be admitted at different levels to make this temperature regulation exact; in any case it is important to keep the reaction temperature so that the gases leave the contact material at a temperature between 400° and 450°.

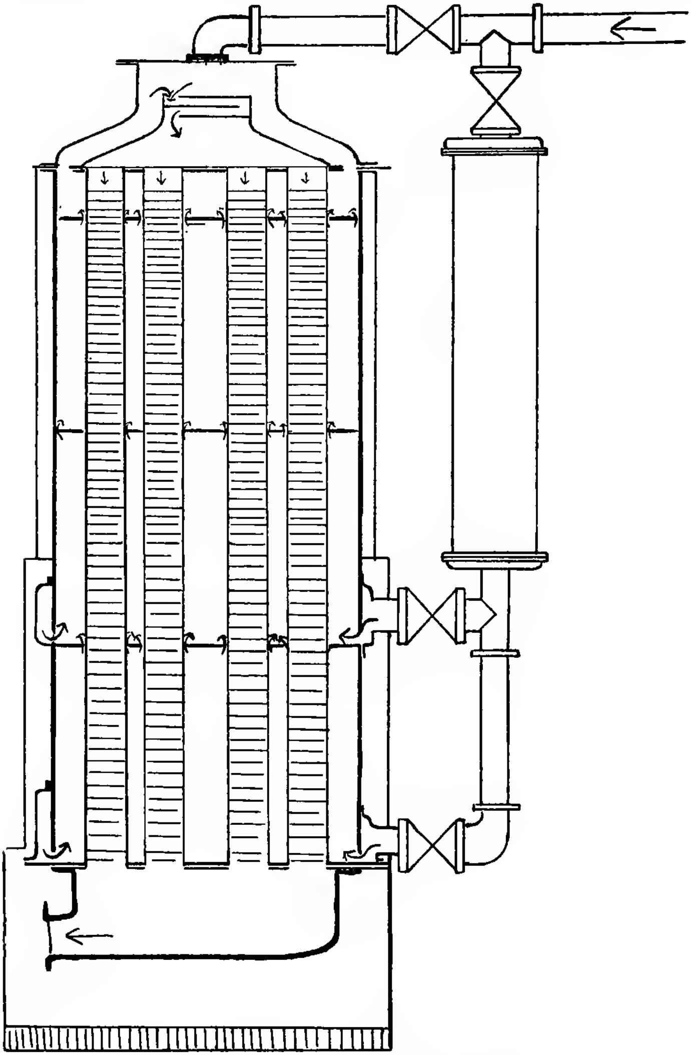


FIG. 16.—The Badische Contact Converter.

Various modifications of this apparatus have from time to time been patented, but the process used is essentially the same.

In the *Schröder-Grillo process* (*Journ. Soc. Chem. Ind.*, 1903, p. 348) a very active catalyst is produced by soaking magnesium sulphate, $MgSO_4.7H_2O$, in a solution of the platinum salt. On heating in the presence of SO_2, the salt puffs up, and finely divided platinum separates. With 5 grams of Pt in this form, one ton of "oleum" ($H_2S_2O_7$) is produced per day, with a loss of only 20 mg. Pt. The dried gases, usually prepared in brimstone burners, are pre-heated to 260°–280°, and are passed into the converter, consisting of perforated iron trays covered with catalyst placed one above the other in a chamber with heat regeneration. The temperature is kept at 350°–400°, and the SO_3, after cooling, is absorbed in a tower with strong sulphuric acid.

In the *Tenteleff process* (1911) used at Petrograd and also in England, the filtered gases are scrubbed with soda or milk of lime to remove HCl, SiF_4, etc.; a heat interchanger is used, and the reaction completed by passing through several nets of platinized asbestos protected from heat loss.

The *Clemm and Hasenbach process*, first used by the Verein Chemischer Fabriken of Mannheim in 1898. Pyrites burner gas is passed over red-hot burnt pyrites (Fe_2O_3 with some CuO), when about 60 per cent. of the SO_2 is converted into SO_3 and all the arsenic is retained by the iron oxide. The lower conversion as compared with the processes using platinum is due to the higher temperature, about 600°, required. Gases containing 2–3 per cent. SO_2 are produced from pyrites in special burners covered with sheet iron to prevent entrance of moist air, and air dried in a sulphuric acid tower is used. Perfectly dry gases do not react, and the amount of moisture must be regulated. The gases enter from four flues into a tall shaft (Fig. 17) containing burnt pyrites at 600° on a revolving hearth, and 60 per cent. of the SO_2 is oxidized to SO_3, which is absorbed by strong sulphuric acid. The dry SO_2 passing on is further converted by platinum in a second converter, often of the Tenteleff type. The spent burnt pyrites is separated at the bottom of the shaft, and fresh burnt pyrites added at the top.

The absorption of the sulphur trioxide at first presented difficulties. When passed through water the SO_3 mist or fog is only slightly absorbed, and it was found best to use concentrated sulphuric acid for absorption, which is then rapid and complete, and fuming acid, or oleum, $H_2S_2O_7$, is formed. Three towers are used, the first containing 98 per cent. H_2SO_4, which is enriched to 25 per cent. SO_3, and then passes to the second tower, where it is brought up to 60 per cent. SO_3. The third tower contains 60 per cent. H_2SO_4, which is brought up to 98 per cent. for use in the first tower.

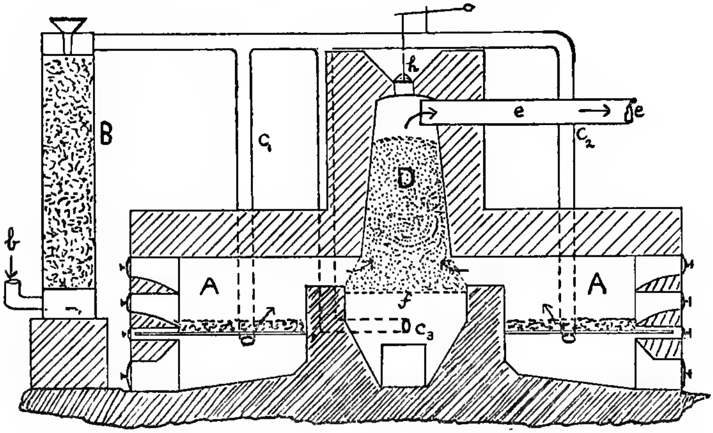


FIG. 17.—Mannheim Contact Plant.

The following commercial products are made :—

(1) Monohydrate, or 100 per cent. H_2SO_4, melting-point 10°.

(2) Oleum, or fuming acid, $H_2S_2O_7$ or $2SO_3.H_2O$, melting-point 34°.

Pure SO_3 melts at 40° ; acids containing from 40–60 per cent. excess SO_3 and from 70–100 per cent. excess SO_3 are solid ; those containing less than 40 and between 60 and 70 per cent. SO_3 are oily liquids.

Fuming Sulphuric Acid, or *Oleum*, $H_2S_2O_7$, is largely used for sulphonating organic compounds, in preparing nitrating acids, and in bringing weaker acids up to 98 per cent. H_2SO_4 without expensive concentrating plant. It is an oily, strongly fuming acid, usually brown in colour owing to the presence of a trace of organic matter. It should not be kept in cast-iron vessels (which however resist the monohydrate), as it permeates and cracks them, but is best stored and transported in vessels of forged iron, which resist acid containing more than 27 per cent. SO_3, and these should not be closed air tight. On account of the possible liberation of hydrogen, empty vessels should not be examined by a naked light until the air has been swept out.

Considerable quantities of acid are made by the contact process; in 1900 the Badische works alone made 116,000 tons. Many new works have been erected in recent years in most countries, including England, as huge quantities of strong acid are required in the nitration processes leading to the production of explosives.

The relative costs of production of 1 ton H_2SO_4 were stated to be, in Germany, for a plant producing 20 tons monohydrate daily, as follows :—

	£	*s.*	*d.*
(1) Old chamber process with hand pyrites kilns ..	1	7	0½
(2) New chamber process with plate towers and mechanical furnaces	1	3	4½
(3) Contact process	1	6	10½

The new chamber processes were then just holding their own; further improvements in the contact process may ultimately oust them, although many new plants are in course of erection. Another defect of the chamber process is that the maximum strength of acid produced by concentrating chamber acid is 98 per cent. H_2SO_4; in modern works the chamber and contact processes are worked together, when acid of any concentration may of course be produced.

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SECTION III.—NATURAL SODA AND THE LEBLANC PROCESS

Natural Sources of Soda.—Sodium carbonate occurs in many mineral waters (*e.g.* Vichy water with 3·8 per cent. Na_2CO_3). It is also found as an efflorescence, known as *natron* or *trona* (Egypt); or *urao* (Mexico), produced by the evaporation of alkaline lakes. In Lower Egypt several thousand tons of *trona*, $Na_2CO_3.NaHCO_3.2H_2O$, are produced annually from *trona lakes*, exported from Alexandria, and used in soap manufacture. This Egyptian natron (formerly called *nitrum*) was known to the ancients, but was not used as a detergent, Neither was soap, made from wood-ashes and tallow, which was apparently used as a pomade (Pliny). There are also *alkali lakes* in the desert east and west of the Rockies, *e.g.* Owen's Lake in California, which is estimated to contain 20–50 million tons, and yields soda by simple crystallization. Recently, important deposits have been discovered in British East Africa, at Magadi, 370 miles from Mombasi, which are 30 sq. miles in extent and estimated to contain 200 million tons. The Magadi Soda Co., formed in 1911, calcine this soda, which gives a "heavy finish" (cf. p. 93) ash containing 99 per cent. Na_2CO_3 with a little iron, which may be separated. The chief difficulty appears to be the cost of transport, but the product is profitably sold to China and Japan.

Ashes of plants growing near the seashore, or salt-springs, are rich in soda (plants from the sea itself yield chiefly potash); such plants are *Chenopodium*, *Salicornia*, *Salsola*, etc. Previous to the invention of the Leblanc process, soda was extracted from the ashes of these plants, and in Normandy and in Spain they are still worked to some extent for soda and other products.

The Leblanc Soda Process.—*History of the Leblanc Soda Industry.*—As already described, the soda used in the manufacture of soap, and other industries, was formerly produced by burning certain marine plants.

At the close of the eighteenth century the French Academy offered a prize for the invention of a process of preparing soda from common salt. In 1787 Nicolas Leblanc, a physician to the Duke of Orleans, discovered such a process, which still bears his name, and he obtained money from his master to erect a works at St. Denis in 1791. In 1793 the Duke was guillotined by the Revolutionaries, and the works were closed. During the period of isolation following the Revolution the supply of soda in France ran short; the Committee of Public Safety compelled Leblanc to make his process known, and handed over the St. Denis works to him. Owing to failing means and health, he was unable to work the factory, and in 1806 he retired to a workhouse, where in his misery he committed suicide. His countrymen decided in 1886 to erect a monument to the unfortunate inventor, whose work has enabled manufacturers in various countries to create a very important and lucrative industry.

After the repeal of the salt-tax in England, the first successful alkali works in the country was erected in Lancashire by Muspratt in 1823, using the Leblanc process. The soda was sold at an extremely low price in order to induce the buyers of natural soda to try the new product. Previous to this, Losh of Walker-on-Tyne had made some soda by the Leblanc process, visiting France during the Peace of Amiens (1802) to get the necessary information. This industry led to the establishment of sulphuric acid, hydrochloric acid, chlorine, and bleaching-powder works, and more alkali works were then erected where deposits of coal and salt were near at hand—at Newcastle-on-Tyne, St. Rollox (Glasgow), Widnes, and St. Helens. These are still in operation under the control of the United Alkali Co.

In 1866 the ammonia-soda process was introduced, and owing to competition the price of soda decreased from £13 to £4 per ton. At present the Leblanc process is not remunerative for the production of soda alone, but is only worked for salt-cake, caustic soda, hydrochloric acid, sulphur, and wet-copper extraction. In 1895, with the introduction of electrolytic processes, another severe blow was given to the Leblanc process. Of late, however, the production of salt-cake (Na_2SO_4) for glass-making by the first part of the process has increased. Only two Leblanc works exist in Germany. The soda industry in Russia is practically confined to the Donetz region, where the salt is mined, on account of the high transport tariff.

The Leblanc Soda Process.—The Leblanc soda process consists of two parts :—

(1) *The salt-cake process,* in which sodium sulphate is produced by heating salt with sulphuric acid—

(i) $NaCl+H_2SO_4 = NaHSO_4+HCl$ (low temperature)
(ii) $NaCl+NaHSO_4 = Na_2SO_4+HCl$ (high temperature)

Large deposits of natural sodium sulphate occur in Persia and the Caucasus, as well as in the water of Owen's Lake, California (see p. 59). It is, however, nearly all made by the salt-cake process.

(2) *The Black-ash process,* in which the salt-cake is heated with limestone and coal to produce sodium carbonate. The work of Kynaston, Gossage, and Scheurer-Kestner (1858–1867) showed, as was later conclusively proved by Kolb, that the reaction occurs, probably in two stages, as follows :—

(i) $Na_2SO_4+2C=Na_2S+2CO_2$
(ii) $Na_2S+CaCO_3=Na_2CO_3+CaS$

Previous theories of the process (*e.g.* Dumas') are incorrect.

In the black-ash process the reduction apparently takes place by the free carbon taking oxygen from the sulphate to form carbon dioxide—

$$Na_2SO_4 \rightleftarrows Na_2S+2O_2$$
$$2C+2O_2 \rightleftarrows 2CO_2$$

Carbon can act as a reducing agent in three ways, according as it forms CO_2, or CO, or CO followed by the combustion of this to CO_2—

$$(1)\quad C+O_2 \rightarrow CO_2+97{,}600 \text{ cal.}$$
$$(2)\quad CO+O \rightarrow CO_2+68{,}000 \text{ cal.}$$
$$(3)\quad C+O \rightarrow CO\ +29{,}650 \text{ cal.}$$

Reaction (2) is the one usually met with ; (3) is important in the blast furnace, and (1) is only concerned in a very few reactions, including the Black-ash process. The heats of combustion per atom of oxygen in the three cases are, respectively, 48,800, 68,000, and 29,650 cals. But the reducing power of a given process is not accurately estimated by the heat of reaction ; it is the available energy which gives a true measure of the affinity (cf. p. 117), and this depends on the temperature and the concentrations of the products. The heats of reaction also depend on the temperature, and the two magnitudes, heat of reaction Q_v, and affinity A have been determined for the three cases :—

$$(1)\quad C+O_2 \rightarrow CO_2$$
$$Q_v=97{,}278+0{\cdot}0041T^2$$
$$A_{(C,\,O_2)}=97{,}278-14{\cdot}63T-0{\cdot}0041T^2+4{\cdot}58T\log\frac{p_{O_2}}{p_{CO}}$$

$$(2)\quad C+\tfrac{1}{2}O_2 \rightarrow CO$$
$$Q_v=29{,}988-3{\cdot}4T+0{\cdot}0077T^2$$
$$A_{(C,\frac{1}{2}O_2)}=29{,}988+7{\cdot}82T\log T-0{\cdot}0077T^2-4{\cdot}61T$$
$$+2{\cdot}29T\log\frac{p_{O_2}}{p^2_{CO}}$$

$$(3)\quad CO+\tfrac{1}{2}O_2 \rightarrow CO_2$$
$$Q_v=67{,}290+3{\cdot}4T-0{\cdot}0036T^2$$
$$A_{(CO,\frac{1}{2}O_2)}=67{,}290-7{\cdot}82T\log T-10{\cdot}02T-0{\cdot}0036T^2$$
$$+2{\cdot}29T\log\frac{p_{O_2}p^2_{CO}}{p^2_{CO_2}}$$

These equations are of considerable importance in the theory of reduction processes, as in metallurgy. If we consider, for instance, the reduction of an oxide—

$$MO+C \rightarrow M+CO$$

the process will occur only when the available energy of the reaction—

$$C+\frac{1}{2}O_2\rightarrow CO$$

is greater than that of the reaction—

$$MO\rightarrow M+\frac{1}{2}O_2$$

The available energy of reactions of the second type cannot usually be given accurately, as very little work has been done on the subject; one usually considers the heat of reaction at absolute zero ($T=0$), which is equal to the available energy at that temperature—

$$A_{T=0}=Q_{T=0}$$

Another method depends on the application of Nernst's theorem ("Thermodynamics," p. 506).

In the Black-ash process, the heat absorbed in the reaction—

$$Na_2SO_4=Na_2S+2O_2$$

is 240,000 cal., which is equal to A at $T=0$. The process occurs in a reducing atmosphere (p_{O_2} small) at a temperature of about 800°, hence if we put $T=1000$ in the equation for $4A_{(C,O_{\frac{1}{2}})}$ we find the available energy to be about 300,000 cal., and therefore sufficient to effect the reduction of Na_2SO_4 to Na_2S.

The Salt-cake Process.—In this process, half a ton of coarse-grain salt is charged into a large hemispherical cast-iron pan, and an equal weight of sulphuric acid, sp. gr. 1·7, from the Glover tower is added from a lead cistern. The pan is heated by hot gases from the hearth or muffle, and 65 per cent. of the HCl escapes through a flue and is absorbed ("pan acid"). The residue is then raked on to an open hearth (Fig. 18), or, in more modern furnaces, into a muffle (Fig. 19), where the second part of the reaction is completed, the mass being stirred by iron rakes. The rest of the acid ("roaster acid") then escapes and is absorbed separately. The residue of *salt-cake*, Na_2SO_4, emitting HCl or SO_3, is discharged into iron trucks.

The pan is made of cast iron with a high combined carbon, but low graphite and silicon, content; it is 10 ft. in diameter, 2 ft. deep, and about 2½ in. thick, the bottom being about 6 in. thick. It rests by a flange over asbestos or other heat-insulator, on a firebrick support, the outlet pipe from the brickwork cover being of stoneware, acid-resisting alloy, or silica. The pan must be very uniformly heated.

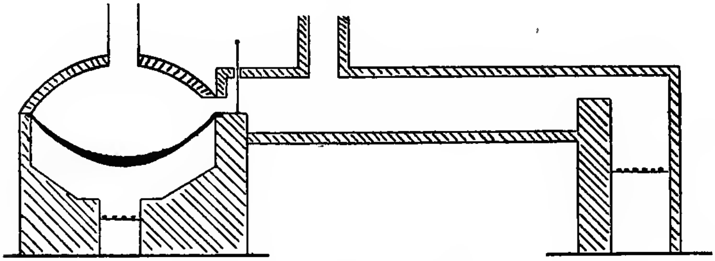


FIG. 18.—Salt-cake Furnace.

The muffle roasters are now preferred to the old open-hearth furnaces, as the products are less contaminated by the fuel used, although the yield of acid from the open hearths was greater. Modern furnaces turn out 85 tons of salt-cake per week.

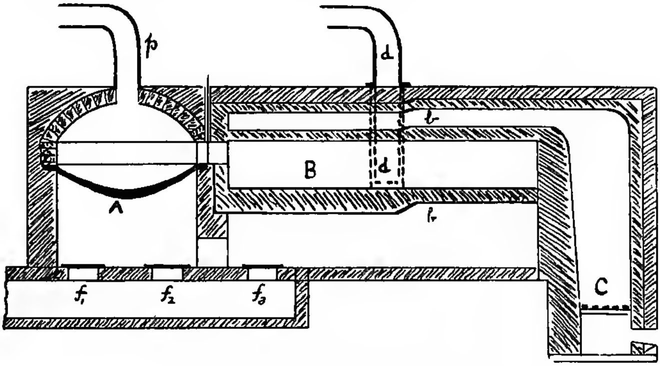


FIG. 19.—Salt-cake Muffle Furnace.

Mechanical furnaces are often used; such as Mactear's (1879), which has a revolving bed with a fixed arch (Fig. 20). The mixture is fed continuously into the middle of the hearth, and is raked by revolving scrapers to the circumference, over which it drops. They are usually fired by coke. These furnaces give a more uniform stream of gas, but require a more elaborate cooling plant for the gas.

Deacon (1876) introduced the "plus pressure" furnace, in which the grate is on a level 5–12 ft. lower than the muffle. The pressure of the ascending column of hot gases balances the suck of the chimney, and prevents leakage from the muffle.

Technical salt-cake contains about 0·3 per cent. free H_2SO_4, 0·1 per cent. Fe, and 0·4 per cent. NaCl. The simultaneous presence of NaCl and H_2SO_4 in the salt-cake is due to the fact that the reaction—

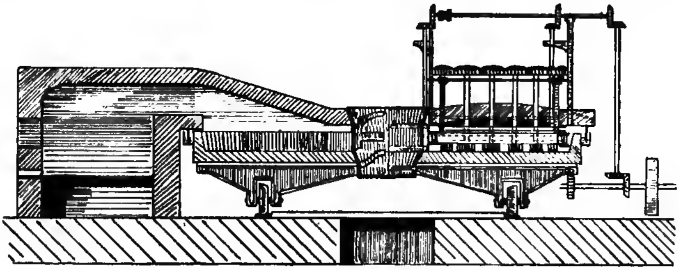


FIG. 20.—Mactear Furnace.

$$2NaCl+H_2SO_4 \rightleftarrows Na_2SO_4+2HCl$$

is reversible, and cannot be quite complete unless an excess of H_2SO_4 is used, when the influence of mass makes itself felt.

The preparation of salt-cake and hydrochloric acid from salt and sulphuric acid is an example of the general method of preparation of an acid. In this, a salt of the acid is acted upon by another acid. A state of equilibrium then results, in which all four compounds are present—

$$RX+HA \rightleftarrows RA+HX$$

The suitability of the method from the point of view of producing pure acid HX will be determined by the following conditions :—

(1) HX is volatile—it is then distilled off by heating

(*e.g.* hydrochloric acid, nitric acid). As HX passes off, more and more is formed to maintain the equilibrium composition, and finally nearly, but not quite, all the HX may be separated.

(2) RA is insoluble—it is then filtered off, and the solution will contain the acid HX. Thus chloric acid may be obtained by precipitating a solution of barium chlorate with sulphuric acid :—

$$Ba(ClO_3)_2+H_2SO_4=BaSO_4+2HClO_3$$

The influence or volatility and of insolubility of a component on the state of equilibrium was clearly recognized by Berthollet, who explained many instances where a reaction apparently went to completion, in this way.

A specially pure variety of salt-cake, containing not more than 0·02 per cent. Fe, is required for glass-making (largely carried out at St. Helens), and is specially manufactured by the Hargreaves process, described on p. 70. If salt-cake is dissolved in water and treated with limestone to precipitate iron, Glauber's salt, $Na_2SO_4.10H_2O$, crystallizes out on evaporation. If fused with coal in "open hearth" roasters, CO_2 is evolved, and the mass thickens—

$$Na_2SO_4+2C=Na_2S+2CO_2$$

On breaking up, lixiviating, and crystallizing, *sodium sulphide*, $Na_2S.9H_2O$, separates. It is used for sulphur dyes, and as a depilatory in tanneries. It should be stored in paraffined or lead-lined steel drums for transport, not in barrels, which it permeates.

Absorption of Hydrochloric Acid.—Formerly alkali manufacturers turned their HCl gas into the air, with such disastrous effects on vegetation and buildings that the Alkali Acts of 1864 and 1874 were passed, according to which alkali manufacturers are compelled to absorb the hydrochloric acid so that the chimney gas does not contain more than $\frac{1}{25}$ grain HCl per cu. ft., or the effluent gas from a sulphuric acid works more than the equivalent of 4 grains per cu. ft. of total acids expressed as SO_3. This absorption is a matter of no difficulty, as the affinity of HCl gas for water is so great that even hot water or steam will condense the greater part of the gas, and coke towers for its absorption were introduced by Gossage as early as 1836 at Messrs. Crosfield's works at St. Helens. They absorbed the hydrochloric acid from 25 tons of salt per day, and so completely that the exit gases produced no turbidity in a solution of silver nitrate.

The hot gases from the salt-cake furnaces at 250° C. are cooled, either by passing through stone tanks or batteries of tubes made of iron, stoneware, or even glass (English works), or through a number of stoneware Woulffe's bottles with a counter-flow of water (Continent). They are then absorbed in large towers, filled with coke, earthenware balls, or perforated discs (Fig. 21). A spray of water descends from the top of the towers. The gases from the pan and roaster are usually absorbed separately, the former giving a purer acid.

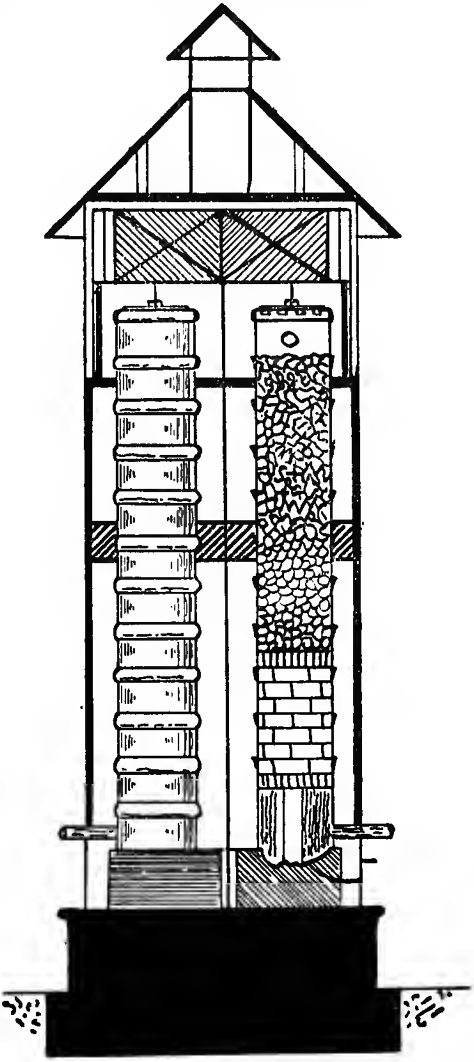


FIG. 21.—Hydrochloric Acid Towers.

The towers are built of sandstone slabs previously boiled in tar, and clamped or bolted together with iron; they are about 60 ft. high. The strength of acid produced (only concentrated acid, about 33 per cent. of HCl, is saleable) depends on the concentration of the gas and the temperature of absorption.

% Conc. HCl in gas by vol.	Temperature of absorption liquid.	% Conc. liquid acid by wt.
100	0° C.	45·2
5	0°	36
10	0°	39
5	20°	33

By the use of acid pumps of stoneware, ebonite, or acid-resisting alloy, the absorption liquid may be circulated, and 33 per cent. acid produced directly, even from weak gases (*e.g.* Hargreaves gas, 10 per cent. HCl by vol.).

The problem of the absorption of a gas by a liquid is somewhat complicated if more than one substance is present in the gaseous phase, but in the case where one constituent is very soluble and the others only sparingly soluble, as when a mixture of hydrogen chloride and air is passed into water, we can deduce the practical results by means of two principles :—

(1) The soluble component in the gas phase will come to equilibrium with that in the liquid, *i.e.* the liquid phase will cease to take up more of the soluble gas, when the partial pressure of the substance in the gas has a certain definite value at a given temperature. The higher this partial pressure, the more concentrated will be the solution in equilibrium with the gas ; in several cases the concentration of the solution is simply proportional to the partial pressure (law of Henry and Dalton)—

$$c_1 = \mathrm{K}p_1$$

With very soluble gases such as HCl, this simple proportionality no longer holds ; in such cases the effect of increased partial pressure is *less* than it should be on the simple law, *i.e.* less gas is absorbed at higher pressures—

$$c_1 = kp^{\frac{1}{n}} \quad (n > 1)$$

(2) The concentration of the solution in equilibrium with the gas phase at a certain partial pressure depends on the temperature, and (with the exception of the gases argon and helium in water, which show a maximum about 20°) it diminishes with rise of temperature, *i.e.* the gas becomes less soluble. In some cases the whole of the gas can be expelled from the solution by boiling (*e.g.* ammonia), but in the case of aqueous hydrochloric acid there is a maximum on the boiling-point-composition curve, and at this point the liquid distils off with unaltered composition. Acids weaker than the maximum boiling-point mixture lose water, those stronger lose hydrochloric acid, until the maximum is reached, and then distil over unchanged. Such an acid is not, however, a definite hydrate, because its composition alters with the total pressure under which distillation occurs.

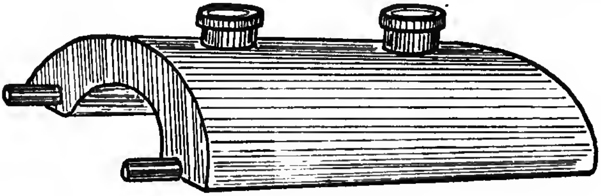


FIG. 22.—Cellarius Receiver.

In Germany the very efficient stoneware *Cellarius receiver* (Fig. 22) is often used instead of towers. Water flows over the saddle; gas goes in and out at the top. These are arranged in series, and water-cooled.

Commercial hydrochloric acid, called *spirit of salt*, or *muriatic acid*, is transported in glass carboys, or in railway tank wagons with waxed-wood linings. It is used for the manufacture of chlorine, and thence of bleaching powder, of chlorates, etc.; in the colour industry; in metallurgy; for purifying coke, iron ores, clay, animal charcoal, etc.; for preparing CO_2; in tinning and galvanizing; in pottery making; for freezing-mixtures (HCl+Glauber's salt); and in conjunction with nitric acid (as *aqua regia*) as a solvent for gold and platinum.

The pure acid may be made by separating the arsenic from the crude acid by washing out the $AsCl_3$ with tar-oils, and then separating the H_2SO_4 and non-volatile impurities by distillation. It is, however, best made by starting with pure salt and sulphuric acid in glass or earthenware retorts, and absorbing in stoneware receivers.

The Hargreaves Process.—In this process (Hargreaves, 1870) a mixture of air, steam and sulphur dioxide is used instead of sulphuric acid to liberate HCl from salt, at a temperature of 400°–500° C.—

$$2NaCl+\underbrace{SO_2+O+H_2O}_{H_2SO_4}=Na_2SO_4+2HCl$$

Possibly, Na_2SO_3 is formed as an intermediate product, and then oxidized. The salt is moistened and allowed to fall on a travelling belt, where it is beaten into a cake 1½ in. thick. This is cut by knives into pieces 3½ in. square, which pass through an oven, from which they emerge dry, and fall off the belt. This preparation of the salt is very important for the proper working of the process, as it is necessary to obtain porous cakes free from powder, which otherwise would choke the converters. These are stacked in kilns of brickwork, or in large cast-iron cylinders 18 ft. diameter and 12 ft. high, ten being used in two rows of five to form a battery. Hot gases from special pyrites burners protected from heat loss, mixed with the requisite amount of superheated steam, pass down the cylinders on the counter-current system, eight cylinders being in action at a time, and two refilling. Fifty tons of salt are put in each cylinder, and the process goes on for three weeks without renewal. The temperature, which is kept up without external heating, must not exceed 600° C., otherwise fusion occurs. The gases are drawn off by a porcelain exhaust, and led to cooling pipes and absorption towers; they contain 10 per cent. HCl by volume. Each battery produces 7000–7500 tons Na_2SO_4 per year, but the process is slow and requires careful working. Still, it has been used successfully in England since 1872, and is also used in France and

Germany. No external heating is required when the process is set going, and economy of fuel is thus effected. For 1 ton salt-cake—

3	cwt. coal are required for the cylinders.
1	,, ,, preparing the salt-bricks.
0·75–1	,, ,, raising steam.
4·75–5	cwt. total.

Up to 8 cwt. may be used, but the consumption of fuel in no case exceeds that used for preparing sulphuric acid and in the salt-cake process, when the latter is used.

It has recently (1907) been proposed to add 0·1–1·0 per cent. copper or iron salts to the salt-bricks to promote the reaction, this of course lowers the purity of the product slightly.

The relative advantages and disadvantages of the Hargreaves process, as compared with the salt-cake process, are as follows :—

Advantages.	*Disadvantages.*
(1) Higher grade of salt-cake.	(1) Greater cost of plant.
(2) Saving in space.	(2) Careful supervision required, and cost of repairs when this fails.
(3) 10*s*. per ton lower process costs.	(3) The HCl cannot be used in the Deacon process, as the SO_2 present in it acts as a catalyst poison.

The Black-ash Process.—The charge used in the black-ash furnaces is—

	Theoretical.	*Practical.*
Salt-cake	100	100
Limestone	79·42	100
Coal	16·9	35·50

The original proportions used by Leblanc were—

Salt-cake	100
Chalk	100
Charcoal	50

The extra limestone and coal are used to allow for impurities, and also to impart porosity to the product, owing to the occurrence of the reaction: $CaCO_3+C=CaO+2CO$ at the last stage of the process.

The *limestone* or *chalk* should be pure, especially free from magnesium. Tyneside works use chalk brought as ballast from the Medway; Lancashire works use the very pure Buxton limestone. The *coal* should have as little ash as possible, but as slack is always used it often contains, after washing, 5 per cent. ash; up to 8 per cent. is tolerated.

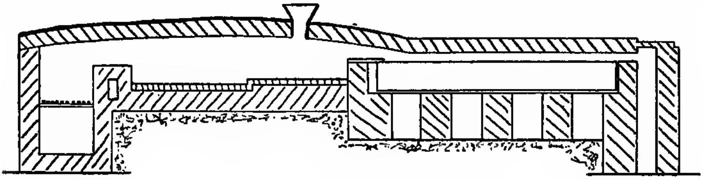


FIG. 23.—Black-ash Furnace.

No reaction occurs till the mass becomes pasty, when decomposition is rapid and complete.

The reaction is still largely carried out in handworked black-ash or "balling" furnaces (Fig. 23), in which the charge is worked on the hearth by men with iron rakes, and is finally worked into lumps or "balls." About 3½ cwt. of salt-cake may be so worked up in an hour. The balls are then taken on iron trucks to the lixiviators.

Elliott and Russell in 1853 introduced revolving furnaces, but these gave too hard an ash. The first successful rotating furnace, or "revolver," was patented in 1855 by Stevenson and Williamson. These revolvers (Fig. 24) are 15–20 ft. long, and are constructed of iron plates lined with firebrick. Those at Widnes and St. Helens are sometimes 30 ft. long

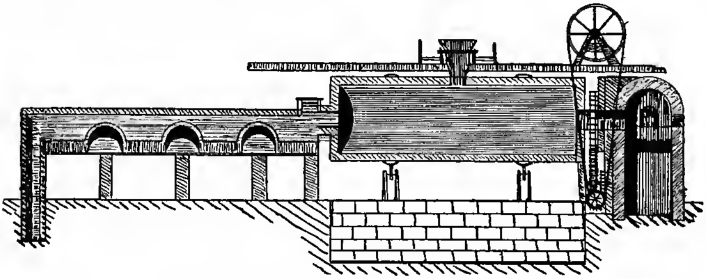


FIG. 24.—Revolving Furnace.

and 12 ft. in diameter. At first the furnace is turned slowly, but finally speeded up to 5 to 6 revolutions per minute. The charge, which is introduced in one batch, consists of 2 tons salt-cake, 2 tons crushed limestone, and 1 ton of coal slack, and the rotation is continued until a yellow flame of carbon monoxide appears. The end-point is judged by an experienced workman, and is a matter of considerable importance. The black-ash is then discharged into trucks, the yield being 1¾ tons per ton of salt-cake. Sometimes a little more salt-cake and limestone are added to make the mass leave the converter more easily. The black-ash is a mixture of sodium carbonate, sodium sulphide (produced by the reaction $Na_2SO_4+4C=Na_2S+4CO$), lime, and unchanged limestone and coal. It is allowed to weather a day or two, when it becomes porous, and is then lixiviated.

Lixiviation is usually carried out in Shanks' lixiviating tanks. These work on the discontinuous counter-current principle, the fresh water being put into a tank containing nearly spent ash, and the concentrated liquors used in leaching the freshly added material. The liquors are conveyed from the bottom of one tank to the top of another by means of siphon pipes with stopcocks.

The conditions for efficient lixiviation are—

(1) The black-ash should be as uniform as possible, so as to lixiviate rapidly and equally.

(2) The lixiviating should be conducted as rapidly as is compatible with complete exhaustion; caustic soda and sodium sulphide are produced on long standing—

$$Na_2CO_3+CaO+H_2O=2NaOH+CaCO_3$$
$$Na_2CO_3+CaS=Na_2S+CaCO_3$$

(3) The temperature in the weak vats should not exceed 35° C., that in the strong vats should not be above 60°. Rise of temperature promotes caustification.

(4) The tank waste should be as completely as possible freed from soluble sodium salts.

The liquors are evaporated, either in pans with hot gases passing over the surface (cf. Fig. 23), or in Thelen pans.

These (Fig. 25) are pans with revolving scrapers. Crude, dark-coloured crystals of carbonate, $Na_2CO_3.H_2O$, then separate, which are fished out with skimmers and recrystallized, to form washing-soda, $Na_2CO_3.10H_2O$, or else calcined to produce soda-ash, Na_2CO_3.

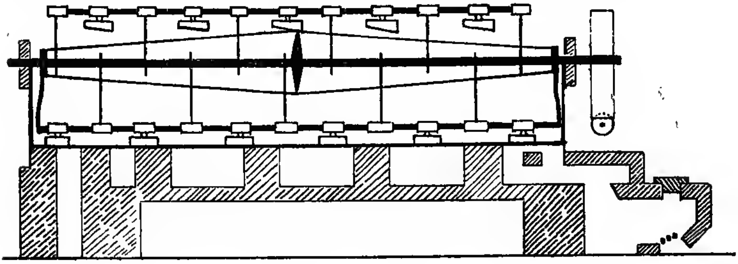


FIG. 25.—Thelen Pan.

In most Leblanc works, however, caustic soda is now produced directly from tank liquor by causticizing with lime (70 to 80 per cent. of the soda in the liquor is present as carbonate), either by mixing with milk of lime in a vessel heated by flue gas or exhaust steam, and provided with mechanical stirrers, or else heating in a tank containing a cage of quicklime, stirring, and blowing in steam (Fig. 26). Air is then blown in to oxidize iron, which settles out, and the caustic liquor is filtered through coke resting on a bed of

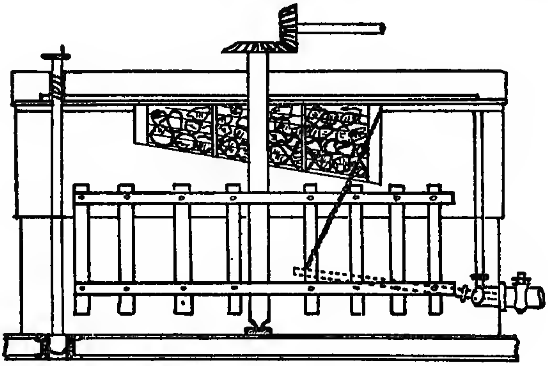


FIG. 26.—Causticizer.

limestone in a tank, under vacuum. In some cases air blowing is used for agitation.

The reaction—

$$Na_2CO_3+Ca(OH)_2 \rightleftarrows CaCO_3+2NaOH$$

is reversible, and it is found that :—

(1) The lower the percentage of carbonate in the original liquor the greater is the conversion to caustic.

(2) The higher the concentration, the less fuel is required.

In practice, a compromise is made by using liquor of such a strength as gives a caustic solution of sp. gr. 1·1, when 91–92 per cent. of the soda is causticized.

The caustic liquor is first evaporated to sp. gr. 1·2 in iron pans heated by the waste heat of the revolver furnace (cf. Fig. 24), 3–4 tons of the 9–10 tons water present per 1 ton caustic in the liquor are thus driven off. The liquor is then run into the soda-pots, which are iron pots 10 ft. in diameter and 6 ft. deep, and boiled down to sp. gr. 1·4–1·5, after which the liquor is allowed to settle, and the clear portion baled out with an iron ladle into another soda-pot, where the evaporation is continued over a free fire until the temperature reaches 400°–500° and the fused caustic has attained a dull red heat. At this point a black scum of graphite, from decomposition of cyanides, separates. To free it from sulphides and cyanides a handful of sodium nitrate is added to each 15-ton batch of caustic at this stage (Ralston, 1860). According to Lunge the reactions are—

(1) $Na_2S+3NaNO_3=Na_2SO_3+3NaNO_2$ (140° C.)
(2*a*) $Na_2S+NaNO_2+2H_2O=Na_2SO_3+NaOH+NH_3$
(2*b*) $Na_2S+2NaNO_2+H_2O=Na_2SO_3+2NaOH+N_2$
(about 152° C.)
(3) $5Na_2SO_3+2NaNO_3+H_2O=5Na_2SO_4+2NaOH+N_2$
(above 360° C.)

The caustic is baled out into iron drums, the last portions being impure. Preliminary evaporation to 100° Tw. is now usually carried out in vacuum evaporators of double or triple effect. Such an evaporator unit is shown in Fig. 27. It consists of a series of tubes contained in an outer jacket and heated by exhaust steam, through which the liquid to be concentrated flows. There is a head at the top, and the foam produced in the tubes, which acquires a rotary motion which assists in separation, here is condensed to liquid and runs off. The steam then passes to the next unit, which is under a higher vacuum (cf. p. 11).

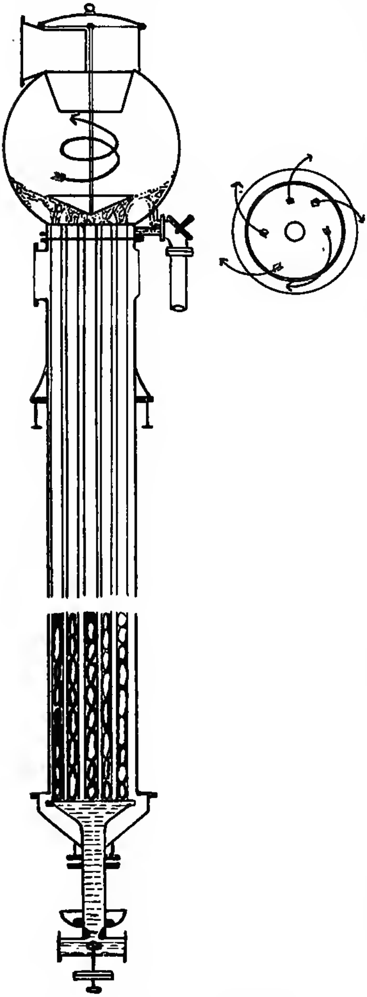


FIG. 27.—Kestner Evaporator.

Solubility Product; Theory of Caustification.—If we consider a solid salt in equilibrium with its saturated solution at a given temperature, we have in the solution not only the molecules of salt, but also the ions produced by electrolytic dissociation of these molecules. Thus, with common salt—

$$NaCl \rightleftarrows Na^{\cdot} + Cl'$$

In the solution there is an equilibrium between the ions and undissociated molecules, and if we assume that the law of mass action applies to ions we shall have—

$$\frac{[Na^{\cdot}][Cl']}{[NaCl]} = K$$

But $[Na^{\cdot}] = [Cl']$, hence—

$$[Na\ ]^2/[NaCl] = K$$

It must be observed that the equation is only very approximately true in the case of strongly ionized salts.

At a given temperature K is constant. But so is the solubility S of the salt, which is assumed to depend only on the undissociated part, hence—

$$[NaCl].K = [Na^{\bullet}][Cl'] = \text{constant}$$

The product $[Na^{\bullet}][Cl']$ is therefore a constant at a given temperature, and is proportional to the solubility S, since the latter is in turn proportional to the concentration of the undissociated salt in a solution containing it alone. If the salt is sparingly soluble, it is practically wholly ionized, and either ionic concentration is equal to the solubility S.

If now Cl' ions are added to the above solution, say by adding hydrochloric acid, the product $[Na^{\bullet}][Cl']$ is increased, and sodium and chlorine ions must be removed by precipitation as sodium chloride to restore the equilibrium value. This is in fact the basis of the usual method of preparing pure NaCl.

The theory of the process of caustification may now be developed from the solubility product formulæ—

$$[Ca^{\bullet\bullet}][OH']^2 = K_1$$
$$[Ca^{\bullet\bullet}][CO'_3] = K_2$$

Then we can see that the causticizing stops when the solubilities of calcium hydroxide and carbonate become equal, and this will occur at a point when a definite amount of sodium carbonate has been converted into caustic. As the carbonate concentration in the solution decreases, the solubility of calcium carbonate will increase, and the simultaneous production of sodium hydroxide will depress the solubility of calcium hydroxide until at a certain point the solubilities of the two solid phases become equal. Then—

$$[Ca^{\bullet\bullet}] = \frac{K_1}{[OH']^2} = \frac{K_2}{[CO'_3]}$$

or

$$\frac{[OH']^2}{[CO'_3]} = \frac{K_1}{K_2} = K$$

With increasing concentration the equilibrium is shifted from the hydroxide side to the carbonate side, because the $[CO'_3]$ concentration is involved simply, but the $[OH']$ concentration as the square. This, as we have mentioned in the preceding section, is in agreement with experience.

Initial concentration of Na_2CO_3.	Temperature.	Percentage caustification at equilibrium.
Normal	100°	99·1
2 Normal	100°	97·8
3 Normal	150°	93·2

The yield is found to be practically independent of the temperature, hence the heat of reaction must be practically zero; on this account no improvement can be anticipated by working at higher temperatures under pressure in an autoclave, although patents for this process were taken out by Parnell in 1877, and failed after extensive trials.

The equations show that a better yield should be obtained with strontia or baryta instead of lime, as the hydroxyl ion concentration is much higher in saturated solutions of these bases than in the case of lime, on account of the larger solubilities, and the solubilities of the carbonates are also less. Thus strontia with a 3 to 4 normal solution of Na_2CO_3 gives 99 per cent. NaOH. In the caustification with strontia heat is evolved, and the yield will thus be increased at lower temperatures—a result which is at first sight quite in contradiction to "practical common sense."

There is always a loss in the caustification of soda with lime, on account of the formation of double salts—

$Na_2Ca(CO_3)_3$ above 40°, *i.e.* in boilers;
$Na_2Ca(CO_3)_3.5H_2O$, below 40°, *i.e.* in filters;

which are sparingly soluble. These double salts are stable only when the liquid phase contains not less than a certain concentration of Na_2CO_3; they are decomposed by pure water. Hence practically all the soda may be removed by repeatedly washing the residue with water (Smith and Liddle, 1881). In practice, 2 per cent. of the soda is left in the lime sludge, partly because complete washing would give too dilute solutions, and partly because a protective layer of $CaCO_3$ appears to form over the particles of double salt.

Similar considerations apply to the lixiviation of black-ash. The lime sludge is used as a "liming" for soils.

Solid caustic soda was first manufactured on a small scale by Tennants at St. Rollox, in 1845. The real manufacture began in 1853 in the Lancashire works, and was only much later introduced on the Tyne, and abroad.

Utilization of Alakli-waste.—Although the nuisance of the escaping acid fumes from Leblanc alkali works was completely overcome by the absorption in Gossage towers, a formidable difficulty remained in the shape of the so-called Alkali-waste, *i.e.* the residue from the lixiviating tanks, which has approximately the following composition:—

Calcium sulphide (CaS)	40
Calcium carbonate ($CaCO_3$)	22
Iron sulphide (FeS)	3
Sand and silicates	15
Soda (Na_2CO_3)	4
Lime (CaO)	10

Each ton of soda produced gives rise to the formation of 1¾ tons of this waste, and enormous heaps accumulated near the Leblanc works, from which by the action of the air and moisture evil-smelling sulphuretted hydrogen was evolved, and dark-coloured polysulphides leached out, polluting the rivers and streams for miles around. In addition, what was perhaps of more consequence to manufacturers, the 20–25 per cent. of sulphur contained in the waste, representing so much costly sulphuric acid, was absolutely lost. In England alone, 150,000 tons of sulphur, valued at £400,000, were thus annually run to waste.

The problem of the utilization of alkali-waste was therefore one on the settling of which the financial success of the Leblanc process came to depend, and repeated attempts were made to arrive at a practical solution.

Besides the manufacture of thiosulphates from the waste, the recovery process of Chance has overcome all difficulties.

Sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is prepared from tank-waste by oxidizing with air, either by blowing air and steam through a suspension of waste in coke towers, or by exposing the waste to the air for a week, with occasional raking, and then lixiviating the product. Calcium thiosulphate is produced, and if this is decomposed by sodium carbonate, the sodium salt is formed. The crystals are used as an antichlor to remove chlorine from bleached fabrics, in photography, in preparing aluminium thiosulphate for use as a mordant, and in wet-silver extraction.

Most of the waste is, however, treated by the sulphur recovery process.

The Chance-Claus Process of Sulphur Recovery.—This process (A. M. Chance, *Journ. Soc. Chem. Ind.*, 1888, p. 162) is practically the only one now used on a large scale for the recovery of sulphur from alkali-waste. Chance in 1888 perfected Gossage's process (1838), in which the waste was decomposed by carbon dioxide. Limekiln gas, as free from oxygen and carbon monoxide as possible, is passed through a suspension of the waste contained in a battery of iron cylinders, called Carbonators. Seven cylinders of 15 ft. by 7 ft., on the counter-current system, are used. Sulphuretted hydrogen diluted with much nitrogen is evolved—

$$(1)\ CaS+H_2O+CO_2=CaCO_3+H_2S$$

This gas is too dilute to utilize directly, so it is passed into a second carbonator of waste, where it is absorbed with formation of calcium hydrosulphide—

$$(2)\ CaS+H_2S=Ca(HS)_2$$

If kiln-gas is now passed through this more concentrated solution, a strong sulphuretted hydrogen is evolved, which is collected in large gasholders (Chance's is 30,000 cu. ft.) over water covered with a layer of oil—

$$(3)\ Ca(SH)_2+CO_2+H_2O=CaCO_3+2H_2S$$

It will be seen that twice as much H_2S is now evolved as in reaction (1), for the same volume of kiln-gas.

The sulphur is now recovered from the H_2S by the catalytic process of Claus (1882). The gas is mixed with air in suitable proportions and the mixture passed to the Claus Kiln, which is a brickwork structure having shelves on which are placed layers of bog-iron ore (hydrated ferric oxide) which acts as a catalyst—

$$(4)\quad 2H_2S+O_2=2H_2O+2S$$

The sulphur is condensed in brickwork chambers in a very pure state, up to 80 per cent. being recovered. The proportions of H_2S and SO_2 in the exit gases are determined throughout the process and the temperature of the kilns is kept low; the temperature of the exit gases should be about 290° C. one foot from the kiln, otherwise loss of S in the gases occurs.

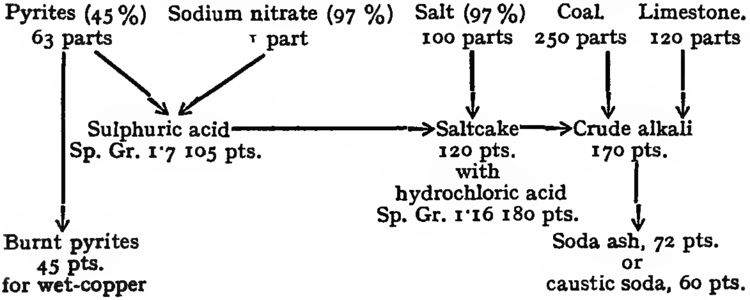
In Europe, 80,000 tons of sulphur are annually recovered by this process; about 35,000 tons in Great Britain alone. In 1904 the United Alkali Co. at Weston Point proposed to use the H_2S by burning it to SO_2, and transforming the latter into sulphuric acid by the contact process. The usual method, however, is to burn the recovered sulphur to produce SO_2 for this purpose. Carbon bisulphide is also made from the sulphur by heating carbon to whiteness in a retort and adding melted sulphur.

The sulphur cycle in the Leblanc Process may be represented as follows:—

$$\begin{tikzcd}
\text{Pyrites} \arrow[r] & H_2SO_4 \arrow[r] & Na_2SO_4 \arrow[r] & \text{CaS (Black-ash)} \arrow[d] \\
& S \arrow[u] & & H_2S \arrow[ll]
\end{tikzcd}$$

From 65 to 80 per cent. of the sulphur is recovered in the cycle; the remainder has to be made good in the form of pyrites.

DIAGRAMMATIC SCHEME OF THE LEBLANC PROCESS.



In 1908, of the total world's production of 2 million tons of soda, only 100,000 tons were made by the Leblanc process. At the same time it must be remembered that this is a declining industry, and much larger amounts were formerly made by the process. The maximum production was in 1879–1883, when 500,000 tons per annum were produced. So much capital is locked up in the process, especially in England, including the chamber acid plants, that the Leblanc process still holds its own, and will no doubt continue to do so for some time. The production of salt-cake, which can be used directly in the manufacture of glass, by the Leblanc process has increased of late. Ultimately the process may be worked only as far as the salt-cake stage, as is the case at present in works using the ammonia-soda process. The production of caustic soda has largely replaced that of carbonate by the Leblanc process, but a new competitor in the shape of the electrolytic processes has recently appeared in this field.

Wet-copper Extraction.—It has already been mentioned that the process of recovering the copper from burnt pyrites used in the manufacture of sulphuric acid forms an integral part of the Leblanc alkali industry. The burnt pyrites, called " Blue Billy " by the workmen, contains up to 3 per cent. of copper, and the latter is recovered by the so-called Wet-copper Process of Longmaid and Henderson, introduced in 1865 at Hebburn-on-Tyne. The ground burnt pyrites is mixed with 12 to 17 per cent. of coarsely crushed rock-salt, and calcined at a dull red heat in long furnaces with shelves. All the copper is converted into cupric chloride, $CuCl_2$. The charge of 2¼ tons per 6 hours is raked during roasting, and the product is lixiviated. The sulphur in the burnt pyrites must exceed the copper by 0·5 per cent.; if it falls below this fresh unburnt pyrites is added. The $CuCl_2$ solution is precipitated by scrap iron, and copper of 70 to 80 per cent. purity is obtained, which is sent to be smelted. The residual oxide of iron is pure enough to be used directly in the steel furnace.

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SECTION IV.—THE AMMONIA-SODA PROCESS; SODIUM, AND SODIUM SALTS

Chemistry of the Ammonia-soda Process.—If carbon dioxide is passed through brine saturated with ammonia, the following reactions occur consecutively :—

(1) $2NH_3+H_2O+CO_2=(NH_4)_2CO_3$
(2) $(NH_4)_2CO_3+H_2O+CO_2=2NH_4HCO_3$
(3) $NaCl+NH_4HCO_3=NaHCO_3+NH_4Cl-2{\cdot}1$ gm. cal.

The sodium bicarbonate, $NaHCO_3$, is sparingly soluble, and its precipitation depends on the value of the ionic-product—

$$[Na^{\bullet}][HCO'_3]$$

at any instant; when the value of this exceeds the solubility product of sodium bicarbonate, *i.e.* the value of the product of the ionic concentrations, $[Na^{\bullet}][HCO'_3]$, in a saturated solution of the pure bicarbonate, then the latter will be precipitated. But the value of the limiting product will be less in a solution of sodium chloride than in pure water, since the solubility of sodium bicarbonate is depressed on account of the forcing back of the ionization of the $NaHCO_3$ by the $Na^{\bullet}$ ions of the NaCl, which is much more strongly dissociated. As the passage of carbon dioxide continues, the second reaction commences, and the influence of mass of the ion HCO'_3 makes itself felt in addition to that of the ion $Na^{\bullet}$. Further precipitation then occurs. Gradually the $Na^{\bullet}$ ions are withdrawn from the solution, and the precipitation ceases when the value of the ionic product $[Na^{\bullet}][HCO'_3]$ is equal to the solubility product. At any given temperature the equilibrium is fixed by the equation of mass action—

$$\frac{[NaHCO_3][NH_4Cl]}{[NaCl][NH_4HCO_3]}=K$$

The maximum yield of bicarbonate is then seen to require—

(1) High initial concentration of $Na^{\cdot}$ ions, *i.e.* saturated brine.
(2) High concentration of NH_3 to facilitate the production of NH_4HCO_3.
(3) Low temperature to diminish the value of the solubility product for $NaHCO_3$.

In practice it is found impossible to realize these conditions completely, owing to the decreased solubility of salt, in presence of ammonia, the dilution of the ammoniacal brine by water vapour carried over with the ammonia gas, and unavoidable rise of temperature. It is therefore necessary to determine what is the most suitable concentration of ammonia, as conditions (1) and (2) are conflicting. The problem has been attacked from the point of view of the Phase Rule, notably by Schreib, Fedotieff, and Janecke. An account of this work will be found in a textbook of the phase rule, *e.g.* Findlay's.

A patent embodying all the reactions involved in the ammonia-soda process was taken out by Dyar and Hemming in 1838, and works erected in Whitechapel, London. These did not pay, and the subsequently erected works of Muspratt at Newton, and of Gaskell at Widnes, were also unable to compete with the Leblanc process. In 1863 Ernest Solvay took out an English patent for an improved process, and in 1865 started a works near Charleroi, the soda being shown at the Paris Exhibition in 1867.

From this time on the industry began to make rapid strides and finally ousted the Leblanc process for the manufacture of sodium carbonate, the latter process now being worked only for salt-cake (Na_2SO_4) and caustic soda.

The actual working of the ammonia-soda process involves many trade secrets, but as far as can be ascertained the general procedure is as follows:—

Description of the Process.—The brine is pumped directly, without preliminary purification, to the *ammonia* *saturators* (Fig. 28), which are towers with a series of diaphragms with serrated inverted cups, or "mushrooms," through which the gas bubbles. Ammonia containing a trace of sulphide may be used with iron pipes, as the latter become coated with a protecting film of sulphide. The temperature must be kept below 60° by suitable means. The final gas may be passed through a second tower, or through a washer to remove ammonia. The final tower is connected with an air-pump to reduce the pressure throughout the whole system back to the ammonia stills.

Carbon dioxide is always present in the ammonia (from the sodium and ammonium bicarbonates present in the mother-liquor from the carbonating tower, from which the ammonia is recovered), and the liquid leaving the ammonia saturator has the following composition :—

	NaCl	NH_3	CO_2
Gr./Lit.	260	80	45

To free it from suspended carbonates of calcium and magnesium, formed from the impurities in the brine, it is allowed to flow to the bottom of a large tank, whence it passes to a second tank, and so on. A clarified liquor of very constant composition is so produced from the hundreds of tons of liquor treated continuously. The mud is passed to the ammonia stills to recover ammonia. The clear ammoniacal brine then passes to the carbonating apparatus, being previously cooled to 30° to prevent loss of ammonia. Two types of carbonating apparatus may be described; the one most used is the first.

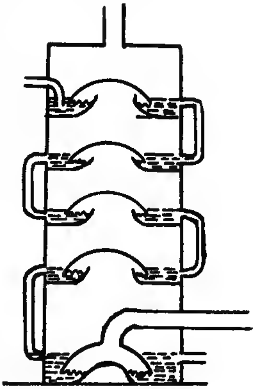

FIG. 28.—Saturator.

(1) *The Solvay Tower.*—The liquor is pumped to the top of a high tower (Fig. 29), 70–90 ft. high and 5–7 ft. in diameter, circular in section, made of iron, and containing a series of baffle plates. Carbon dioxide pumped in at the base meets the descending ammoniacal brine, and in the lower part of the tower there are Cogswell coolers (1887),

consisting of mild-steel tubes expanded into plates in the central parts, through which cold water flows. Usually the carbonation occurs in two stages :—

(i) Formation of $(NH_4)_2CO_3$;
(ii) Formation of NH_4HCO_3 and precipitation of $NaHCO_3$.

Each stage is carried out in a separate tower, and the temperature in the second tower is kept at 20° C. so as to produce a bicarbonate of the proper consistency. In all cases, hard crusts of bicarbonate form in the second tower and gradually choke it. Such towers are then changed over to the first stage of the process, when the crusts dissolve.

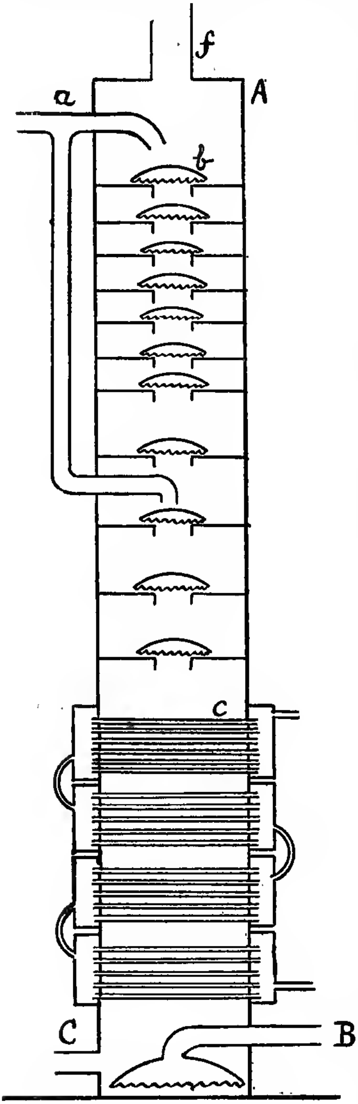

Fig. 29.—Solvay Tower.

(2) *The Honigmann Carbonator.*—In this (Fig. 30) there are three or more conical iron vessels with coolers, which are filled with ammoniacal brine, and then carbon dioxide is pumped through, meeting the liquid on the counter-current principle. When the conversion in one vessel is completed, the contents are blown out to the filter, and fresh ammoniacal brine added. 8–12 tons of bicarbonate may be produced in 6–9 hours. The advantages of this plant compared with the Solvay are

absence of crust-formation and less resistance to gas-flow, with consequent saving on the compressors; its disadvantages are the intermittent working in an otherwise continuous process, and the lower absorption efficiency (80–90 per cent., as against 90–95 per cent. CO_2 absorbed in the Solvay).

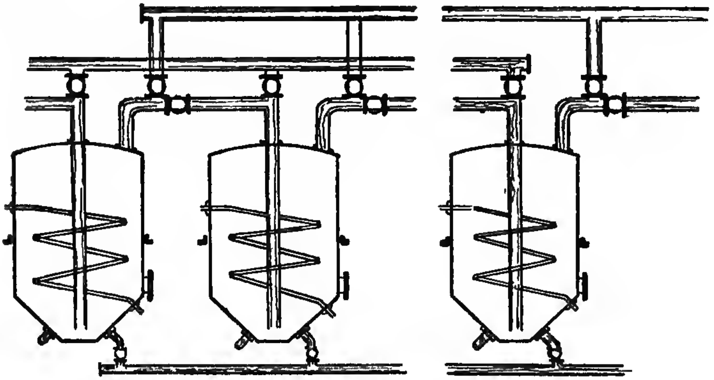

FIG. 30.—Honigmann Apparatus.

The carbon dioxide used in the carbonization is obtained from two sources:—

(i) The *Lime Kilns*, where limestone is burned to produce lime, CaO, for the decomposition of the ammonium chloride in the mother-liquors.

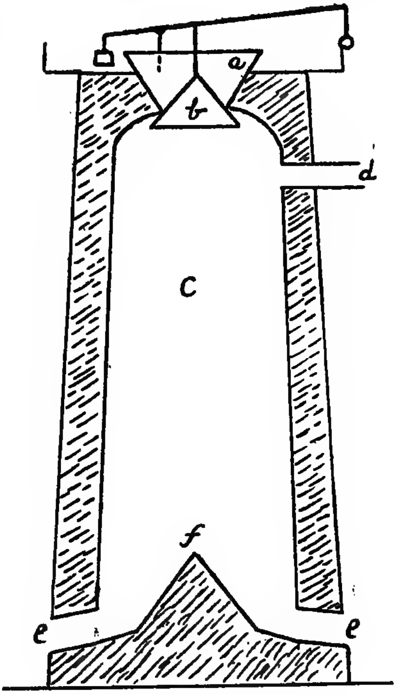

FIG. 31.—Lime Kiln.

A typical kiln is shown in Fig. 31. An intimate mixture of limestone with the least amount of coke requisite for burning is fed into the "cup and cone" at the top of the kiln, whence it drops slowly down. The conical hump at the bottom, called the "dumpling," prevents the accumulation of dust and assists in the even distribution of air, which passes in through the openings at the bottom, from which the quicklime is also removed. The kiln gas is sucked through two scrubbing towers filled with coke, down which is sent a spray of water to remove dust, tar, and sulphur dioxide from the coke. The proportion of coke to limestone is very important as regards the concentration of the gas:—

Cwt. coke per ton lime.	% CO_2 in gas.
6	31
4·5	35
3·0	40

(ii) Calcination of the bicarbonate to produce soda-ash.

Lime-kiln gas contains up to 40 per cent. by volume of CO_2, calciner gas 90–98 per cent. A mixture of the two containing 53 per cent. CO_2 is used in the carbonation of the ammoniacal brine.

The magma of bicarbonate and mother-liquor issuing from the carbonating apparatus is filtered by means of a *rotary filter* (Fig. 32), consisting of a perforated drum covered outside with flannel and evacuated inside, which dips into the trough containing the paste. The layer of bicarbonate collecting on the flannel is washed with water, and scraped off by knives as the cylinder revolves. By this washing the mother-liquor is somewhat diluted, and it receives some sodium bicarbonate; it contains practically all the ammonia originally present in the ammoniacal brine. This ammonia is recovered in the ammonia stills, in which the liquor is first treated with steam, to drive out free ammonia and decompose carbonate, and then with milk of lime (prepared by slaking the lime from the kilns in large iron boilers with an internal screw to push on the lime) to set free the ammonia from the ammonium chloride. The ammonia is driven out with steam. The *stills* consist of iron towers with diaphragms similar to the saturators, milk of lime being added halfway up and exhaust steam at the base of the tower. The ammonia gas is cooled to 57°–60° and re-enters the cycle in the ammonia absorbers. Some trouble owing to choking of the towers by lime is experienced. The liquor from the ammonia stills contains all the chlorine of the salt in the form of calcium chloride—

$$2NH_4Cl + Ca(HO)_2 = 2NH_3 + H_2O + CaCl_2$$

Practically all this was run to waste in the early days of the Solvay process; the liquors are now often evaporated and the calcium chloride used for dust-laying, in refrigerators, and in some chemical processes. Attempts to prepare free chlorine from the ammonium chloride have been made, *e.g.* Mond's magnesia process described in Section VI.

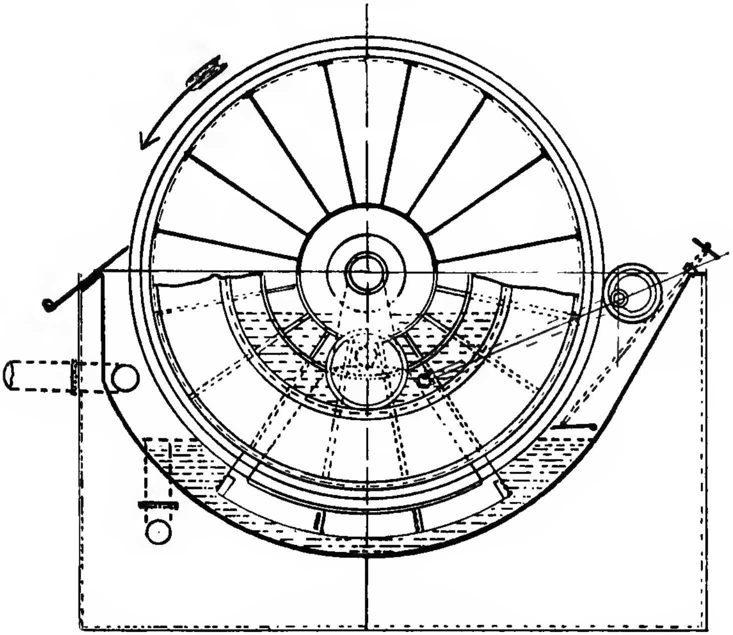

Fig. 32.—Rotary Filter.

The bicarbonate is then decomposed at a fairly high temperature in *Thelen pans* (cf. Fig. 25) 30–50 ft. long, heated externally by a fire at one end or by gas. The flue gases traverse the whole exterior of the pan, and rocking scrapers inside push the bicarbonate slowly forwards until it is finally discharged to a mill, and then goes to sacks on a weighing machine in the form of soda ash, which should be of 99–99·7 per cent. purity, containing a trace of NaCl. Revolving furnaces 60 ft. long are sometimes used instead of Thelen pans.

The consumption of raw materials per ton of soda ash produced is as follows: Coke, 1·3 cwt.; limestone, 1 ton 4 cwt.; coal, 10 cwt.; ammonia, 5 lbs.

If sodium nitrate is used instead of chloride in the ammonia-soda process, it is possible to precipitate nearly all the sodium as bicarbonate, and the technically important ammonium nitrate may be recovered from the mother-liquor up to 87·5 per cent. theory—

$$NaNO_3+NH_4HCO_3=NH_4NO_3+NaHCO_3$$

Soda Crystals or Washing Soda, $Na_2CO_3.10H_2O$.—This is prepared by dissolving soda ash in a mild steel vessel with steam, a little salt-cake (Na_2SO_4) being added to make the crystals harder. The solution is made up to sp. gr. 1·2–1·3 at 100°, is treated in settling tanks with a little bleaching powder to oxidize any organic matter and precipitate iron, and after standing the clear liquor is siphoned off to large semicircular mild steel crystallizing pans. The crystals take 7–10 days to form, and are drained in a hydro-extractor. If a hot solution is allowed to crystallize, the monohydrate $Na_2CO_3.H_2O$ separates; it is known as *crystal carbonate*, and contains more than double the percentage of soda in washing soda.

Bicarbonate of Soda.—This is prepared from the raw product by boiling with water to expel ammonia (and nearly half the CO_2), recarbonating, and drying in a current of hot air or carbon dioxide.

Concentrated Soda Crystals.—This product, $Na_2CO_3.NaHCO_3.2H_2O$, has the same composition as natural *trona*, and is prepared by crystallizing a solution of equivalent amounts of carbonate and bicarbonate at 35°. It is neither efflorescent nor deliquescent, and is used in wool-washing.

If a denser form of soda ash (" heavy finish ") is required, it is prepared by calcining the product from the Thelen pan in a Mactear furnace till the apparent density is increased from 0·16 to 0·3.

Caustic Soda by Löwig's Process.—Much sodium carbonate from the ammonia-soda process is made into caustic soda by the process of Löwig (1882), originally introduced for solutions, but extended by Mond and Hewitt (1887) to the direct conversion of solid soda ash. In this process the carbonate is roasted at a red heat with water-gas in a " revolver " furnace with ferric oxide, when sodium ferrite is produced and carbon dioxide evolved—

$$(1)\quad Na_2CO_3+Fe_2O_3=2NaFeO_2+CO_2$$

The mass is then broken up, cooled, and thrown into hot water, when a concentrated solution of caustic soda is formed and ferric oxide regenerated and precipitated—

$$(2)\quad 2NaFeO_2+H_2O=Fe_2O_3+2NaOH$$

The caustic solution is evaporated in pans in double or triple effect vacuum apparatus, being finally fused in an iron pot over a free flame at 400°–500°, when it is poured into iron drums and sealed up, or it may first of all be powdered. 10–15 tons are fused at a time. The concentrated liquor obtained in this process results in a saving of 60 per cent. of the evaporation per ton of caustic, over the lime method.

The causticizing may also be effected with lime, as in the Leblanc process.

The Ammonia-Soda Industry.—The Solvay works in England are situated at Northwich, Plumbley, Lostock-Gralam, and Winnington, in the Northwich district, and at Sandbach near Crewe—all being owned by Brunner, Mond & Co. The works at Winnington is the largest in the world, and is on the site of the first English works erected in 1872 by Dr. Ludwig Mond. This firm controls practically all the works using the process in Europe and America. The only independent works in England is that of the United

Alkali Co. at Fleetwood, Lancs. There are several works in America outside the combine, *e.g.* Michigan Alkali Co., Columbia Chemical Co., etc., and a new works at Trieste was recently started. Solvay works exist in Belgium, at Dombasle in France, in Russia (Lubimoff and Solvay works at Berezniak, near Ousolia, on the banks of the Kama), and Germany (Deutsche Solvay Werke). Some soda is produced in Italy.

The production of sodium carbonate by the ammonia-soda process is shown in the following table, which indicates the rapid expansion of the industry :—

1864–1868	300 tons.
1902	1,600,000 ,,
1916	3,000,000 ,,

The important competitors of the Ammonia-soda process are (i) the natural soda deposits of Magadi, which however have to be transported great distances with corresponding cost; and (ii) the electrolytic processes, which if used exclusively would lead to great over-production of chlorine. It is therefore in a fairly secure position, although the disposal of the calcium chloride is an awkward problem which still has to be solved.

Soda from Cryolite.—In 1849 Julius Thomsen, of Copenhagen, found that the mineral cryolite, $3NaF.AlF_3$, found in large quantities in the Bay of Ivitût in South Greenland, is easily decomposed by lime ; in 1857 a manufacturing process was started, which was taken over in 1865 by the Pennsylvania Salt Manufacturing Co. of Natrona, near Pittsburg, by whom it is now solely controlled. A mixture of 100 parts of finely ground cryolite with 150 parts of chalk, together with a little calcium fluoride as a flux, is heated in thin layers on iron plates short of fusion and lixiviated hot—

$$2(AlF_3.3NaF)+6CaO=6CaF_2+Al_2O_3.3Na_2O$$

The solution of sodium aluminate obtained is decomposed by passing in carbon dioxide, when alumina is precipitated in a granular form containing 20 per cent. Na_2CO_3, and this must be often washed with hot water to extract all but a residual 2 per cent.—

$$Al_2O_3.3Na_2O+3CO_2+3H_2O=3Na_2CO_3+2Al(OH)_3$$

A very pure sodium carbonate is obtained by evaporating the solution, and the alumina can be used for the manufacture of alum, aluminium sulphate, or aluminium.

Scheele's Process.—In 1773 Scheele found that if a solution of sodium chloride is boiled with lead oxide, caustic soda is produced—

$$2NaCl+4PbO+H_2O=2NaOH+3PbO.PbCl_2$$

The difficulty, however, is to recover the lead oxide in a suitable form. Bachet found that the oxychloride can be decomposed by lime-water—

$$3PbO.PbCl_2+Ca(OH)_2=4PbO+CaCl_2+H_2O$$

Berl and Austerweil state that if the oxychloride is treated with successive quantities of lime-water, a residue containing 98·86 PbO and 1·03 CaO is left, which can be used again for decomposing more sodium chloride. The process may find some application on the large scale. The equilibrium $K=\frac{[OH']^2}{[Cl']^2}$ shows that the yield is independent of the concentration. With too concentrated solutions, however, the litharge becomes coated over with insoluble oxychloride. The yield may amount to 50 per cent. with $\frac{N}{2}$ NaCl and the correct amount of PbO.

Sodium.—Metallic sodium (and to a much smaller extent potassium) is prepared in large quantities by the original process of Davy, *i.e.* electrolysis of fused sodium hydroxide, the methods adopted subsequently to Davy's experiments (distillation with carbon, iron, etc.) having gone quite out of use on the large scale. The principal firms are the Castner-Kellner Co. at Weston Point and Newcastle-on-Tyne in England, Clavaux in France, the Niagara Electrochemical

Co. in America, and the Elektrochemische Fabrik Natrium at Rheinfelden in Germany, In the Castner process (1891), fused sodium hydroxide contained in the iron pot A (Fig. 33) is electrolyzed at a temperature below 330° by the anode B, of resisting material such as nickel, and the iron cathode C, the top being insulated by asbestos from the pot A. After starting, the heat developed by the current is sufficient to keep the mass fused. Sodium separates in D, and floats to the top of the tubular iron vessel with a wire-gauze extension surrounding the cathode, whence it is ladled out from time to time by a perforated iron spoon, which allows the fused caustic to run through but retains the sodium. The metal usually comes into the market in the form of thick rods, soldered up in tins.

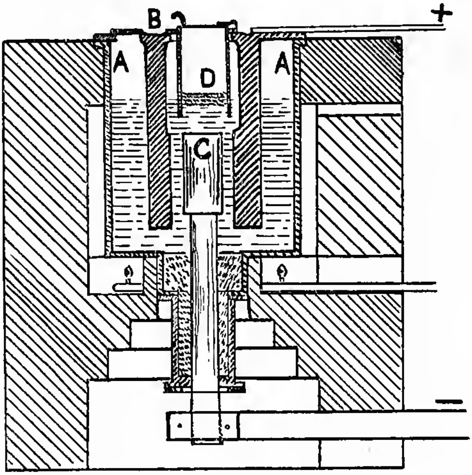

Fig. 33.—Castner Sodium Apparatus.

At Niagara a combination of the Acker and Castner processes is used, molten sodium chloride being used as electrolyte in the first part of the process, with a fused lead cathode, with which the sodium alloys. The alloy is then passed into a second space, where it is made the anode in fused caustic soda ; sodium dissolves out of the alloy, and is deposited on the cathode. The caustic soda remains unchanged. In this way sodium is obtained at less than 1*s.* per lb. A mixture of NaOH and Na_2S in equal parts, NaOH being continuously added, has also been proposed as electrolyte.

The world's production of sodium in 1905 was 350,000 tons. It is used chiefly in the preparation of sodium peroxide, silicon, magnesium, and organo-metallic compounds in the aniline-dye industry. Prior to 1880 large quantities were used in the manufacture of aluminium, which is now made entirely by electrolysis.

Sodium Peroxide.—Sodium peroxide, Na_2O_2, is prepared by Castner's process (1891). Sodium contained in aluminium trays is heated to 300° in a long iron tube-retort, through which a current of dry air free from carbon dioxide is passed—

$$2Na + O_2 = Na_2O_2$$

It is a yellowish-white substance, usually sold as a powder, which reacts energetically with water, giving off oxygen. With ice-cold water it forms a hydrate, $Na_2O_2.8H_2O$. In the fused state it is a powerful oxidizing agent, "opening up" many refractory minerals, *e.g.* with chromite, $FeCr_2O_4$, it gives Fe_2O_3 and Na_2CrO_4. In solution it is used for bleaching textile fibres; in the case of wool the NaOH formed must be neutralized as fast as it is produced with dilute H_2SO_4 or acetic acid. It is also used in confined spaces (*e.g.* diving-bells) for purifying air, since carbon dioxide is absorbed and oxygen liberated. It costs about 1*s.* 6*d.* per pound.

Merck prepares pure hydrogen peroxide from sodium peroxide by adding the calculated amount in small quantities at a time to cooled 20 per cent. sulphuric acid, and after separating the solution from the crystals of sodium sulphate, distilling in vacuum.

Borax.—Borax, or sodium pyroborate, $Na_2O.2B_2O_3.10H_2O$, or $Na_2B_4O_7.10H_2O$, is found in lakes in China, Persia, and Tibet, whence it reaches Europe as *tincal.* It is prepared to some extent from the boric acid obtained from the volcanic gases escaping from *suffioni,* or steam-jets, in the Tuscan marshes. Deposits occur in California, and much borax is made by decomposing the minerals—

Boracite, $2(Mg_3B_8O_{15}).MgCl_2$, of Stassfurt,
Colemanite, $Ca_2B_6O_{11}.5H_2O$, of California,
Borocalcite, CaB_4O_7, of the Argentine,

with boiling sodium carbonate solution.

Much borax is now made from the Boronatro-calcite, $Na_2B_4O_7.2CaB_4O_7.18H_2O$, of Chili.

Octahedral borax, $Na_2B_4O_7.5H_2O$, is prepared by cooling a solution of sp. gr. 1·26 to 70°, and collecting all crystals forming above 56°, at which temperature ordinary borax separates. Electrolytic methods of preparing borax by electrolyzing a solution of boric acid in brine with a carbon anode and lead cathode separated by a porous diaphragm were proposed in 1906 by Levi.

Refined borax costs about £18 a ton. It is used in brazing, to keep metallic surfaces clean, as most metallic oxides dissolve in fused borax, many with the production of characteristic colours. It is also used in the dye industry, and in glazing porcelain.

Sodium Perborate.—If boric acid is mixed with sodium peroxide, and the mixture added slowly to cold diluted sulphuric acid, sodium perborate, $Na_2B_4O_8.10H_2O$, separates. The crystals may be washed with alcohol and dried at 50°. Carbonic acid may be used instead of sulphuric. Sodium perborate is largely used as a bleaching detergent, mixed with soap or other substances; it is made on a large scale by adding 150 lbs. Na_2O_2 to 200 lbs. ice and water, and then adding 150 lbs. boric acid; chimney gases (CO_2) are then blown through, and the crystals separated. The last portions are separated by saturating the mother-liquors with common salt. Electrolytic processes are also used.

Sodium Silicate, Soluble Glass, or Water Glass.—Sodium silicate is prepared by melting together 23 parts of soda ash and 45 parts of powdered quartz, with 25 parts of coal-dust, in reverberatory furnaces. The glassy product is dissolved in 56 parts of water in an autoclave. The thick liquid so produced is used as a fireproofing material, for making joints with asbestos, as an adhesive for glass and porcelain, for preserving eggs and stone, for making artificial stone, and for adding to soaps.

Large quantities of sodium silicate solution are also made by the so-called *wet method*, which has the advantage of yielding a more uniform product. Powdered silica, preferably in the form of infusorial earth, is digested with caustic soda solution of sp. gr. 1·22–1·24 under 3–4 atm. in an autoclave, the heating being effected by blowing in steam for about 3 hours and stirring. The liquor is then evaporated in iron pans to sp. gr. 1·7; 2·8 parts infusorial earth are used for 1 part NaOH.

Sodium Phosphate.—Ordinary sodium phosphate is $Na_2HPO_4.12H_2O$, and is obtained from bone ash, $Ca_3(PO_4)_2$, by digesting with dilute sulphuric acid, when phosphoric acid is produced, and neutralizing the latter with soda ash. It is used in preparing enamel, in soldering, as a weighting material in dyeing, and medicinally.

Sodium Chromate and Dichromate.—Sodium chromate, Na_2CrO_4, is prepared by heating powdered chromite, or chrome-ironstone, with soda ash and lime in presence of air—

$$2FeCr_2O_4+4Na_2CO_3+4CaO+7O = Fe_2O_3+4CaCO_3+4Na_2CrO_4$$

The melt is lixiviated with water and made slightly acid with acetic acid. On evaporation lemon-yellow crystals of Na_2CrO_4 separate. If the solution is made slightly acid with sulphuric acid instead of acetic acid, and evaporated, the very soluble and deliquescent red dichromate, $Na_2Cr_2O_7$, separates. If this is heated with potassium chloride in solution, NaCl separates, and potassium dichromate, $K_2Cr_2O_7$, crystallizes on cooling in fine orange-red crystals. The potassium salt may also be obtained directly if potassium carbonate is used in the fusion. Nearly all the potassium dichromate is produced in England, but of late it has been largely replaced by the cheaper and more soluble sodium salt. Chrome ironstone occurs in the Urals, in Asia Minor, California, and Australia.

Chromates and dichromates are used as mordants, as oxidizing agents in the manufacture of aniline black, and in preparing chromate pigments (*e.g.* chrome yellow, $PbCrO_4$).

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SECTION V.—ELECTROLYTIC PROCESSES

Electrolytic Processes.—The electrolysis of a solution of sodium chloride was carried out by Cruickshank in 1800; further experiments were made by Davy, Berzelius and Hisinger, and others, on the decomposition of saline solutions by the electric current, but it was not until 1885 that successful industrial application was made of these discoveries. With the invention of the dynamo, the possibility of carrying out many chemical reactions on a large scale by the electrolytic method became clear, and numbers of patents have been taken out from that time till the present day. The main types of processes used on the large scale in the electrolytic production of alkali and chlorine fall, however, into four groups, and representatives of each group will be described here.

I. Cells using fused sodium chloride as electrolyte: The Acker Process.
II. Cells using a solution of sodium chloride with a suitable diaphragm to separate the anode and cathode: The Griesheim Process; Hargreaves-Bird Process.
III. Cells with a solution of sodium chloride with a moving mercury cathode to remove the sodium produced: The Castner-Kellner Process.
IV. Cells with a solution of sodium chloride in which the denser caustic soda solution sinks by gravity: The Bell or "Glocken" Process.

Certain newer types of cell combine the principles of two of the above groups; such a cell is the Billiter-Leykam patent.

General Principles of Electrolytic Processes.—According to Faraday's law, 96,540 coulombs (1 coulomb is the quantity of electricity conveyed by a current of 1 ampere in 1 second) liberate one gram-equivalent of an ion, *e.g.* 23 grams of sodium, or 35·5 grams of chlorine, or 31·5 grams of divalent copper. Thus 58·5 grams of sodium chloride are decomposed by 96,540 coulombs. This fundamental quantity of electricity is called a *faraday*, and one faraday therefore liberates one gram-equivalent of any ion, provided there are no complications in the electrolytic process. Thus, if a solution of copper sulphate is electrolyzed, then at a certain concentration hydrogen may be liberated together with the copper, and the sum of the equivalents of the copper and hydrogen liberated by 1 faraday will be unity.

The extent of chemical decomposition is quite independent of the voltage applied to the cell, but in order to decompose an electrolyte with actual liberation of the ions in the ordinary chemical condition, *e.g.* chlorine gas, a definite voltage must be applied, since the products of electrolysis accumulating at the electrodes set up themselves a voltage in the opposite sense to the applied voltage, and this back E.M.F., as it is called, must be overcome before any current will pass and therefore any decomposition occur. In the most favourable circumstances the applied voltage must be at least equal to the sum of the electrode potentials of the two ions at the concentrations at which they are present at the electrodes, but this is only when the decomposition occurs reversibly, and in practice where irreversible processes always occur to some extent, a higher voltage must be applied. The cost of the power supplied electrically depends not only on the current, but also on the voltage at which it is used, and the power consumption is measured in kilo-watts—

$$1 \text{ kilowatt} = 1000 \text{ watts} = 1000 \text{ volt-amperes}$$

The energy consumption is measured in kilowatt-hours; 1 kilowatt-hour being the energy supplied by 1 kilowatt in 1 hour, *i.e.* the unit of energy is the product—

$$1 \text{ volt} \times 1 \text{ ampere} \times 1000 \times 60 \times 60$$

The current is measured by an ammeter in series with the main circuit, the voltage by a voltmeter connected across the terminals of the electrolytic cell, and the power consumption may then be determined from the readings of the two instruments, or may be determined separately by a wattmeter.

The general arrangement for electrolysis is shown in Fig. 34. D is the dynamo producing the current, R is a regulating resistance, A is the ammeter, V the voltmeter, and C the electrolytic cell.

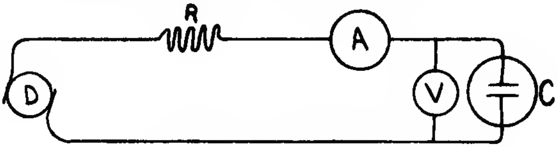

FIG. 34.—Electrolysis.

If several electrolytic cells are used they may be connected in series (A in Fig. 35), or in parallel (B in Fig. 35), or in a combination of series and parallel, called multiple-arc (C in Fig. 35), according to requirements.

According to the mode of connection the current through the cells may be varied with a constant value of the applied voltage of the dynamo. Thus if each cell has a resistance of 5 ohms, and the applied voltage is 25 volts, then if four cells are used—

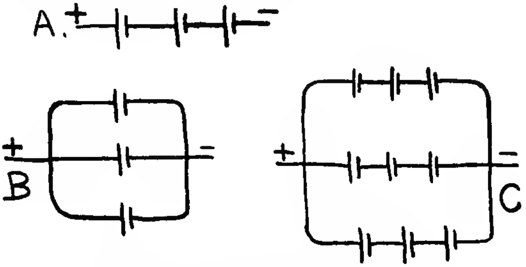

FIG. 35.—Electrical Connections.

(i.) In series: $C=25/4\times5=25/20=1{\cdot}25$ amperes;

(ii.) In parallel: $C=25/5\div4=100/5=20$ amperes;

(iii.) In two groups of two in series:

$$C=25\Big/\left(\frac{10}{2}+\frac{10}{2}\right)=25/10=2{\cdot}5 \text{ amperes}$$

The terminal voltage is equal to the applied voltage, *i.e.* the voltage of the dynamo, minus the watts lost in the cell$=E-CR$. In the three cases considered above the reading of the voltmeter connected with the cell terminals would be in all cases when it was connected with the extreme terminals, 25 volts, but if it was connected with say the second cell in the series of four, the voltmeter would give the reading $25-5\times 1{\cdot}25=18{\cdot}75$.

It is the aim of the electrochemist to arrange the electrolytic process so that, in the first place the power consumption shall be as small as possible, and in the second place so that the process shall proceed as smoothly as possible, that is, that secondary processes do not occur and large changes of voltage and current do not appear during the progress of the operation. The voltage will usually be fixed, and it is necessary to ensure that changes of the current do not occur to any appreciable extent; thus the concentration of the electrolyte must be kept nearly constant throughout the course of the electrolysis, and the cells are usually connected in parallel.

The Current-efficiency of the process is the percentage of current which is usefully employed in the process, and is calculated from the actual yield as compared with the theoretical yield according to Faraday's law.

We shall now pass on to a more detailed account of the different types of cells. Further information as to the subjects of this chapter may be found in the books on Electrochemistry.

Cells with fused Electrolyte.—After several unsuccessful attempts by inventors to electrolyze fused salt on a large scale, the *Acker process* was started at Niagara in 1900. In this process fused salt, with or without the addition of fluorides to promote fusibility, was used over a cathode of molten lead or tin, which formed an alloy with the sodium liberated. This alloy was run out of the electrode space, and decomposed by blowing steam through it, when fused caustic soda was produced. The voltage applied was 6·75, the current efficiency was 54 per cent. On account of the high temperature the consumption of electrodes was great. In 1907 a fire started, and the works was destroyed. It has not been reconstructed.

Cells with Solutions and Diaphragms.—(*a*) *Griesheim-Elektron Type*—extensively used in Germany, France, Russia, and Spain.

In the various works using this type of cell 33,000 H.P. are expended, with the production of 70,000 tons of caustic soda and 120,000 tons of bleaching-powder. The cells are formed (Fig. 36) of a number of porous diaphragms fitted into an iron tank, lined inside with cement, by means of iron slides like window-frames. The composition of the diaphragms is nominally secret, but as an illustration the patent of Breuer (1884) may be mentioned, in which cement is mixed with salt and cast into slabs. When these are placed in water the salt dissolves out leaving a porous mass. The anode cell is rectangular; usually six to twelve are used. Sheet-iron plates form the cathodes, the tank being connected with them, and the anodes are of carbon. Such electrodes are usually made of artificial graphite, manufactured by the Acheson Graphite Co. at Niagara by heating coke in an electric furnace; electrodes of Fe_3O_4, fused in the arc and cast, are also used. The cell is surrounded

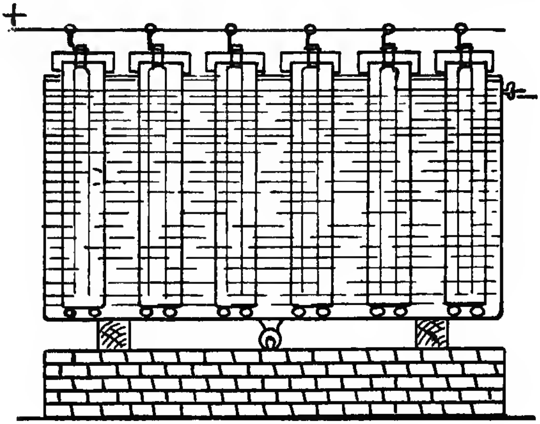

FIG. 36.—Griesheim Cell.

by a steam jacket, and the brine is run into the anode chambers through pipes in the lids. Chlorine is led off through a second lot of pipes to a main. The cathode tank is provided with a run-off cock for the caustic liquor. The temperature is maintained at 80°–90°, the current density 100–200 amperes per sq. metre, the voltage 3·5–4·0, all the cells being in parallel. Diaphragms of silicated asbestos are largely used in America with this type of cell.

(*b*) *The Hargreaves-Bird Cell.*—This cell is largely used at Middlewich in Cheshire. The cells (Fig. 37) are narrow rectangular boxes, the top and bottom of which are of cast-iron, and the sides are made of silicated asbestos to serve as diaphragms, which are 0·1 in. thick. Outside the diaphragms, and in close contact with them, are the cathodes of copper gauze or perforated sheet copper. The anodes consist of lead cores, on which are strung rough blocks of gas-carbon, the lead being covered in with cement where it is exposed. Brine is fed in at the bottom and the spent liquor run off at the top. The sodium ions pass through the diaphragm, which is impervious to sodium chloride, and sodium is deposited on the cathode. Either steam or a mixture of steam and carbon dioxide is blown on the cathode surfaces, which are enclosed in an iron box, and either caustic soda or sodium carbonate is formed, the concentrated solutions running off at the bottom to vacuum evaporators. Chlorine escapes through the pipes at the top, and is led to the bleaching powder chambers. Each cell has 10 sq. m. cathode, and decomposes 106 kilos. NaCl per 24 hours, with 2300 amperes at 4·5 volts. The current efficiency is 97 per cent.

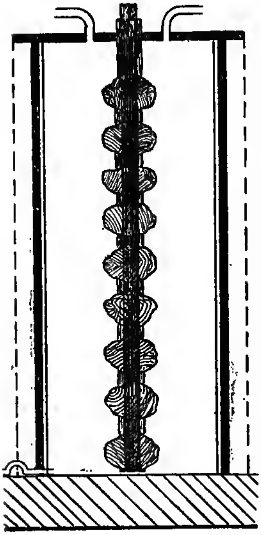

FIG. 37.—Hargreaves-Bird Cell.

Cells with Moving Mercury Cathodes.—Such cells are the Castner and Castner-Kellner types. The difficulties formerly encountered in the use of diaphragms led Castner in America and Kellner in Austria to devise cells without diaphragms, in which metallic mercury is used as cathode, as in the earliest experiments of Davy, and forms an amalgam with the sodium liberated. This amalgam is then treated with water, when a solution of caustic soda, and hydrogen, are produced. The mercury then passes back to the cathode compartment. The early *Castner-Kellner*, or "Rocking-table" cell (Fig. 38), which is still in use, consists of a shallow slate tank, divided into three compartments by slate partitions which do not quite touch the floor. The floor of the tank is covered with mercury, which seals the three compartments. Each end compartment is filled with strong brine, the middle one with water. In the original Castner cell the mercury was the cathode, and by giving a rocking motion to the cell by means of an eccentric, the amalgam flowed to the central compartment, where it was decomposed by the water. Kellner introduced an iron cathode in the inner compartment, and thus utilized the E.M.F. generated there. In the latest types of cells the tables are fixed, and the mercury is circulated by an Archimedean screw, finally dropping over a cascade into water to free it from sodium, after which it re-enters the cycle. Anodes of platinum gauze are now used instead of carbon. The current efficiency is 90 per cent., the voltage is 4·3. Large works using the Castner-Kellner cells exist at Niagara Falls; a

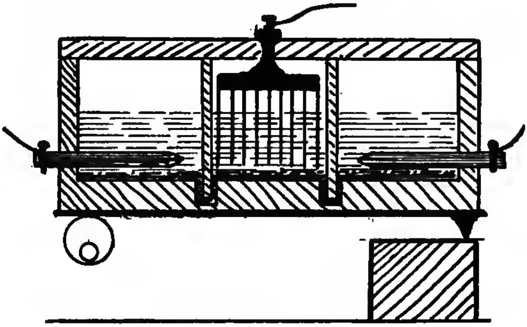

FIG. 38.—Castner-Kellner Cell.

smaller works is in operation at Weston Point, near Liverpool. The advantages of the process are the purity of the alkali, the high concentration of caustic solution produced, the high current efficiency, and the absence of secondary reactions. Its disadvantages are the high voltage, the cost of the mercury, of which 72 tons are required for a 6000 H.P. plant, and the high cost of erection.

Gravity Cells.—In these the separation of the anodic and cathodic liquids is effected by their different densities. A familiar type is the "Glocken," or Bell, cell (Fig. 39) of the Chemico-Metallurgical Co. of Aussig (Austria), in which the anode and cathode are separated by an inverted bell of non-conducting material. The anode is carefully adjusted at the proper height inside: the cathodes are iron plates. The dense NaOH solution falls down and is run off by a cock, brine entering continuously into the bell. Chlorine escapes through the lid. A smaller type of this cell is now made, 25,000 of which are required for 3000 H.P.

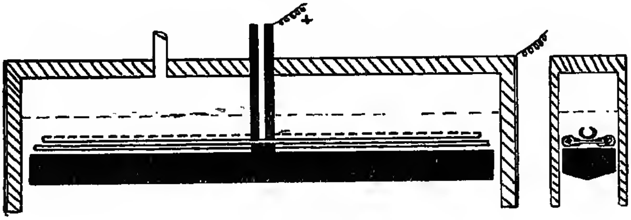

FIG. 39.—Gravity Cell.

Billiter-Leykam Cell.—This is a combination of the diaphragm and bell types. The bell is made small, and is closed at the bottom with a nickel or iron net on which rests a sheet of asbestos cloth surmounted by a powder composed of an insoluble substance such as alumina or barium sulphate, mixed with asbestos wool and made into a paste with brine. The carbon anode is placed inside the bell, and brine is introduced above the diaphragm and flows through it. The cell is heated to 85°, and has a current efficiency of 92 per cent. It is said to work very satisfactorily.

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SECTION VI.—THE MANUFACTURE OF CHLORINE AND DERIVED PRODUCTS

Chlorine.—The industrial methods of preparing chlorine, are—

(1) The oxidation of hydrochloric acid—
  (*a*) By the action of manganese dioxide.
  (*b*) By the action of nitric acid.
  (*c*) By atmospheric oxygen, in presence of catalysts.
(2) Electrolysis of chlorides, especially sodium chloride.
(3) From salt, sulphuric acid, and manganese dioxide.
(4) From magnesium chloride.

Process (1) (*a*) is used in connection with the manganese recovery process of Weldon; process (1) (*c*) is the Deacon process; the electrolytic processes include the Acker, the Griesheim, the Castner-Kellner, and the so-called " Glocken " or bell type. The rest of the processes, except possibly one type of (4), are no longer in use on a large scale. Although some chlorine is made in small works by process (3), it is usually more convenient to buy liquid chlorine in steel cylinders from the large manufacturers.

The Weldon process.—In this process chlorine is obtained by oxidizing crude concentrated hydrochloric acid from the saltcake furnaces (which should contain as little sulphuric acid as possible to avoid formation of calcium sulphate in a subsequent stage of the process) with commercial manganese dioxide in the form of the mineral Pyrolusite (75 to 85 per cent. MnO_2) in the first instance, and with recovered manganese dioxide in the further working of the process. Pyrolusite is found in Germany, Bohemia, Spain, Russia, India, Australia, Japan, and the United States. Most of that used in Great Britain comes from South Russia. Softer ores are preferable to hard ones, and the ore is sold on the percentage of MnO_2 it contains, as the lower oxides of manganese are less efficient and carbonates waste hydrochloric acid. The ore is broken up into pieces of suitable size and charged into the chlorine stills (Fig. 40), made in this country of a special sandstone found at Southowram, and hence called "Yorkshire Flag." Other stone found at Heworth, near Newcastle-on-Tyne, requires boiling in tar to render it impervious. Suitable stone is found in Germany, but the finest natural acid-resisting material is the volvic lava of Puy-de-Dome (France), already referred to in connection with the concentration of sulphuric acid. This comes into the market in the form of blocks and slabs ready for use. Substitutes for volvic lava are "Obsidianite," made by Davison & Co., Buckley, near Chester, and "Nori" ware, made by the Accrington Brick and Tile Co. These materials have the advantages of cheapness and resistance to high temperatures.

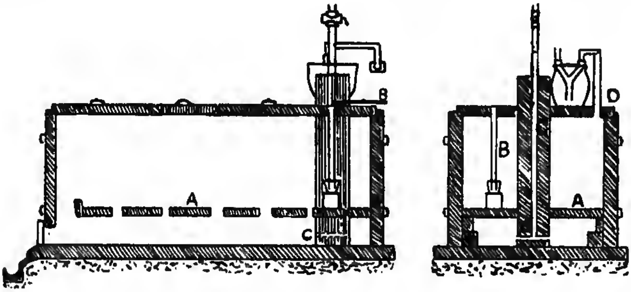

Fig. 40.—Chlorine Still.

The flags forming the stills are joined at the edges by bevels or otherwise, the joints being tightened by putty or rubber cord. The inside measurements are 7 ft. by 5 ft. by 3 ft., and upwards. Six to ten cwt. of ore are placed through a manhole on the false bottom A, and the acid run in through the pipe B. Steam is blown in cautiously at intervals through the lead pipe C, terminating in a stoneware column, having at the top a tap protected from chlorine by a water-seal. The gas is evolved through the pipe D, which also has a water-seal in the pot. After 24 to 48 hours the reaction is complete, and the still-liquor is run off into the Weldon plant for recovery of the manganese. It is still acid, as complete oxidation is never attained. The oxidation appears to go best with 28–30 per cent. acid.

The Weldon process was begun by Walter Weldon in 1866, at Gamble's works in St. Helens, and in 1869 the manufacture commenced. The principle of the method is as follows.

The acid solution of manganese and ferric chlorides from the stills is agitated with limestone or ground chalk in the well A (Fig. 41), where free acid is neutralized and ferric hydroxide precipitated. The liquor is pumped into iron tanks B, and allowed to settle. To the settled liquor, run off into the oxidiser C, about 10 ft. diameter by 30 ft. deep, milk of lime is added in 30–40 per cent. excess of that required to precipitate all the manganese as $Mn(OH)_2$. This addition of excess lime is the vital point of the process, as Gossage in 1837 had failed through adding only the theoretical amount of lime. The mixture is now warmed to 55°–60° by steam, and air blown through for about 2½ hours by a powerful blowing engine. The compound $CaO.MnO_2$, or calcium manganite, is precipitated. By adding more still liquor and continuing the blowing, this is converted into $CaO.2MnO_2$, which is run out into the settlers D, allowed to settle out, and then run off as a thin mud—" Weldon mud "—into the special stills E. Complete oxidation of MnO to MnO_2 can, as Weldon found, take place only in presence of strong bases, such as lime, because MnO_2 has acid properties, and in the absence of bases will combine with unchanged MnO to form $MnO.MnO_2$ or Mn_2O_3, but more slowly than with lime. About 168 cu. ft. of air at normal pressure is required to convert 1 lb. MnO to MnO_2; this is about 13 times the theoretical amount.

The Weldon stills, sometimes called " Octagons " from their shape, are usually much larger than the ones previously described, say 7 ft. by 7 ft. by 8 or 9 ft. high, or in large works 12 ft. high and wide, and octagonal in shape. The cover is dome-shaped, has an inlet for steam and an outlet for Cl_2. The chlorine is carried off through stoneware pipes, and is dried by passing through cooling pipes, or even through a sulphuric acid tower. The mud is run in at the top through a funnel, the acid halfway up through a pipe, and the waste liquor out at the bottom back to the recovery plant.

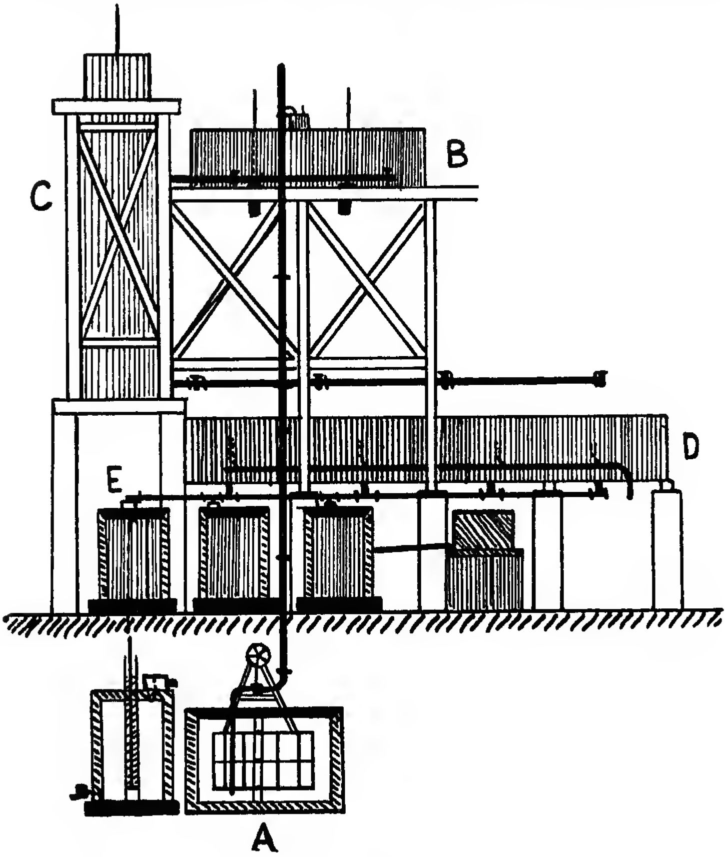

FIG. 41.—Weldon Plant.

Constant testing of the products at each stage of the process is necessary for proper working. The efficiency is 45 to 70 cwt. salt (NaCl) per ton of bleaching powder (37 per cent.), taking the first and last products, which works out at less than 32 per cent. on the chlorine. Fresh MnO_2 to the extent of 3 parts for every 100 parts of bleaching powder made must be added, by working it through ordinary stills as described, to cover losses.

The theory of the Weldon process has not been completely elucidated; it is probably somewhat as follows. When manganese dioxide is dissolved in cold concentrated hydrochloric acid a dark brown solution is obtained, which appears to contain $MnCl_4$. If this is diluted with water, hydrolysis occurs, and manganic hydroxide, $Mn(OH)_4$, is precipitated. Hence the acid used in the process must not be too dilute.

$$(1)\ MnO_2+4HCl=MnCl_4+2H_2O$$

If the dark solution is warmed it breaks up into chlorine and a solution of manganous chloride—

$$(2)\ MnCl_4=MnCl_2+Cl_2$$

The further reactions of the process are usually formulated as follows:—

$$(3)\quad MnCl_2+Ca(OH)_2=Mn(OH)_2+CaCl_2$$
$$(4)\quad Mn(OH)_2+Ca(OH)_2+O=MnO_2.CaO+2H_2O$$
$$(5)\quad MnO_2.CaO+CaO+MnCl_2+O=CaO.2MnO_2+CaCl_2$$

Half the chlorine of the hydrochloric acid used is therefore always wasted in the form of calcium chloride. The oxidation in the Weldon process is effected by the change of the tetravalent manganese ion, $Mn^{\bullet\bullet\bullet\bullet}$, formed in reaction (1), to the divalent ion $Mn^{\bullet\bullet}$, with simultaneous liberation of two chlorine ions in the form of elementary chlorine—

$$Mn^{\bullet\bullet\bullet\bullet}+2Cl'\rightarrow Mn^{\bullet\bullet}+Cl_2$$

The electro-affinity of chlorine is 1·35 volt, hence the available energy absorbed in the formation of Cl_2 from $2Cl'$ is $2\times1{\cdot}35\times23{,}046$ cal.$=62{,}224$ cal. (cf. "Thermodynamics," p. 479). The electrode potential of the reaction $Mn^{\bullet\bullet\bullet\bullet}\rightarrow Mn^{\bullet\bullet}$ is 3·20 volt, and the affinity is therefore $3{\cdot}2\times23{,}046=73{,}747$ cal., which indicates that tetravalent manganese is a powerful oxidizing agent (cf. Abegg, " Handbuch der anorg. Chem.," vol. iv. p. 804). This exceeds the absorption of available energy for the formation of chlorine by 11,500 cal., and the reaction therefore occurs spontaneously, even in the cold.

The regeneration of manganese in the process depends on the further oxidation of the divalent manganese ion by atmospheric oxygen in presence of the hydroxyl ions from the lime—

$$Mn^{\cdot\cdot}+2OH' \rightleftharpoons Mn(OH)_2$$
$$Mn^{\cdot\cdot}+2OH'+H_2O+\tfrac{1}{2}O_2 \rightleftharpoons Mn^{\cdot\cdot\cdot\cdot}+4OH'$$
$$Mn^{\cdot\cdot\cdot\cdot}+4OH' \rightleftharpoons Mn(OH)_4 \rightleftharpoons MnO_2+2H_2O$$

The chief point to be attended to in practice is the proportion of " base " to manganese dioxide in the resulting mud. By " base " is understood all constituents of the mud which neutralize acid, leaving behind pure MnO_2 (Lunge). The following results (from Lunge) show the progress of the operation in different stages, the proportions of constituents being in equivalents :—

1st operation : charging the oxidizer and adding the lime—

$$100MnCl_2+160CaO=100MnO+60CaO+100CaCl_2$$

2nd operation : blowing—

$$\begin{aligned}&100MnO+60CaO+86O\\&\quad=86MnO_2+14MnO+60CaO\\&\quad=48CaO.MnO_2+14MnO.MnO_2+12CaO.2MnO_2\\&\quad=86MnO_2+74(CaO \text{ and } MnO)\end{aligned}$$

3rd operation : final addition of still liquid—

$$\begin{aligned}&48CaO.MnO_2+24MnCl_2\\&\quad=24CaO.2MnO_2+24MnO+24CaCl_2\end{aligned}$$

4th operation : second blowing—

$$24MnO+12O=12MnO.MnO_2$$

Apart from the calcium chloride there remain—

From the 2nd operation

$$14MnO.MnO_2+12CaO.2MnO_2$$

From the 3rd operation $24CaO.2MnO_2$
From the 4th operation $12MnO.MnO_2$
Altogether $26MnO.MnO_2+36CaO.2MnO_2$
or $98MnO_2+36CaO+26MnO$

Hence from 100 equivalents of MnO originally employed, and 24 added in the third operation, there are obtained—

(1) 98 equivalents MnO_2 instead of 124 possible, *i.e.* 79 per cent.

(2) 62 equivalents bases, viz. $36CaO+26MnO$.

By adding the final still liquor in operation (3) the proportion of MnO_2 to MnO has been lowered from 86 to 79 per cent., but the bases have been diminished even more, viz. from 74 to 62, which is the important point.

The Weldon process may proceed improperly, owing to faulty working, in two ways, named after the properties of the mud obtained :—

(1) "Foxy," or "red," batch—obtained by blowing too hard before adding a sufficient excess of lime in the first operation, when free MnO is oxidized directly to red Mn_3O_4, as in the original unsuccessful procedure of Gossage before the excess of lime was introduced by Weldon. There is no cure for this when once the red batch has appeared, and it must be worked up in the stills, with consequent loss of acid.

(2) "Stiff" batch—obtained by insufficient air blast, too high a temperature, or too much lime. The mud then becomes crystalline and very stiff, and tends to choke the blast. The cure is to put on the full force of the blast at once, and add more still liquor to dissolve the excess of lime.

The Deacon Chlorine Process.—After earlier unsuccessful work, H. Deacon and F. Hurter, from 1868 on, evolved a process for the direct oxidation of hydrochloric acid by atmospheric oxygen in presence of a catalyst—

$$4HCl+O_2 \rightleftarrows 2H_2O+2Cl_2$$

The catalyst used is cupric chloride, and according to Hurter its action is simply as follows :—

(i) $2CuCl_2 \rightarrow Cu_2Cl_2 + Cl_2$
(ii) $2Cu_2Cl_2 + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$

In any case, it is clear that the Deacon process involves the partition of hydrogen between chlorine and oxygen. Experiments on this reaction in the gaseous state at the high temperatures produced by explosion were made by Harker ("Inaug. Diss.," Tübingen, 1892); further measurements with a view to elucidating the mechanism of the Deacon process were made by Lunge and Marmier (1897), G. N. Lewis (1906), and von Falckenstein (1907), all of which are referred to in Haber's "Thermodynamics." At the temperature at which the reaction is carried out, the affinity of hydrogen for oxygen is greater than its affinity for chlorine. As a measure of the affinity is taken the available energy A; the reasons for the adoption of this magnitude rather than the heat of reaction Q, formerly used, depend on the following characteristics of chemical affinity :—

(1) It must depend reciprocally on at least two substances, and on the products of their interaction.

Thus, we can speak of "the affinity of hydrogen for oxygen to form water," or "the affinity of oxygen for hydrogen to form water," both phrases having exactly the same meaning. Such expressions as "the affinity of oxygen," or "the affinity of oxygen for hydrogen," are quite meaningless, as the products may be different, *e.g.* steam, or hydrogen peroxide.

(2) It is a function of temperature, pressure, and often of the nature of the medium in which the reaction occurs.

(3) It is affected by the masses of the interacting substances according to the law of mass action.

It must be noticed that the "affinity" as understood in (2) and (3) is not quite the same as that considered on p. 38, but the latter, which is the real affinity apart from other factors, cannot at present be measured.

(4) When the numerical measure of the affinity is positive,

the given reaction can occur; when it is negative, the opposite reaction; when zero the interacting substances are in equilibrium with the products of the reaction.

(5) Affinity is elective, *i.e.* if the affinity of X for Y to form XY is greater than the affinity of X for Z to form XZ, then XY is formed preferentially to XZ in the system composed of X, Y, and Z.

Of these conditions, (1) and (2) are satisfied by the heat of reaction Q, but not the others; all are satisfied by the available energy A, which is in this case often called the *affinity*.

The equation of mass action—

$$\Sigma n_1 \log [A_1] = \log K$$

applied to the Deacon process, gives—

$$\frac{[H_2O]^2 \times [Cl_2]^2}{[HCl]^4 \times [O_2]} = K$$

or if partial pressures are used—

$$\frac{p^2{}_{H_2O} \cdot p^2{}_{Cl_2}}{p^4{}_{HCl} \cdot p_{O_2}} = k, \quad \text{or} \quad \frac{p^{\frac{1}{2}}{}_{H_2O} \cdot p^{\frac{1}{2}}{}_{Cl_2}}{p_{HCl} \cdot p^{\frac{1}{4}}{}_{O_2}} = k' = \sqrt[4]{k'}$$

From the experiments referred to above, Haber has calculated the following table:—

Temperature °C.	k' obs.	k' calc.	Observer.
352	4·02	4·57	Lewis.
386	3·02	3·40	,,
419	2·35	2·62	,,
430	2·5	2·42	Lunge and Marmier.
450	2·26	2·10	v. Falckenstein.
480	2·0	1·73	Lunge and Marmier.
600	1·52	0·90	v. Falckenstein.
650	0·794	0·728	,,
1537	0·123	0·133	Löwenstein.

The values of "k calc." were obtained from the equation (1)—

$$4 \log k' = \log \frac{p^2{}_{H_2O} \cdot p^2{}_{Cl_2}}{p_{O_2} p^4{}_{HCl}} = \frac{5961}{T} - 1{\cdot}86 \log T + 0{\cdot}000722T - 2{\cdot}17$$

which was derived by Haber from various considerations.

The same considerations as to temperature and yield hold in the case of the Deacon process as in the contact process for sulphuric acid (see p. 45). The reaction is accompanied by evolution of heat, and increase of temperature diminishes the yield in equilibrium. At low temperatures, however, the reaction does not occur sufficiently rapidly, and an optimum temperature must therefore be fixed. This has long been known empirically, and is 400°–500°. Probably 450°–460° is the best temperature; below this the velocity is too small to give a satisfactory yield, whilst above it volatilization of cupric chloride (which can never be avoided) becomes excessive.

Many experimental details of value in large scale working will be found in the work of Lunge and Marmier, which is fully considered in Haber's book.

In the Deacon process we have an excellent illustration of the application of a *catalyst;* unless we can find some substance which can speed up the velocity of the reaction so that it attains its equilibrium values at low temperatures, where these equilibrium values are favourable to the yield, the process could not be worked, as the equilibrium values corresponding to the high temperatures at which the normal reaction velocity (without catalyst) is appreciable are too small to be of value. In cases where the reaction is endothermic, the equilibrium value increases along with the velocity on rise of temperature, and this difficulty does not arise (*e.g.* formation of NO from air in the arc).

The *yield* in the Deacon process may be calculated similarly to that in the contact process for SO_3 (p. 43).

If x is the fraction of the HCl decomposed, giving $\frac{x}{2}$ mols. Cl_2 and $(1-x)$HCl—

$$\frac{[Cl_2]}{[HCl]}=\frac{x}{2(1-x)}$$

If we put—

$$\frac{p^{\frac{1}{2}}_{H_2O}\cdot p^{\frac{1}{2}}_{Cl_2}}{p^{\frac{1}{4}}_{O_2}\cdot p_{HCl}}=\sqrt[4]{k}=k' \ .$$

then

$$k'=\frac{x}{2(1-x)}\cdot\frac{1}{p^{\frac{1}{4}}_{O_2}}\sqrt{\frac{[H_2O]}{[Cl_2]}}$$

or, if the initial gases are dried, as is always the case, $\frac{[H_2O]}{[Cl_2]} = 1$, and then—

$$\frac{x}{2(1-x)} \cdot \frac{1}{p^{\frac{1}{4}}_{O_2}} = k'$$

Excess of oxygen is therefore favourable to the yield, but since the partial pressure enters the product as the fourth root, it will have little effect on the result; an increase of the oxygen pressure 18 times only increases the yield from 60 per cent. to 75 per cent.

In the experiments of Lunge and Marmier, dry mixtures of hydrochloric acid with air or oxygen were passed over broken bricks soaked in a solution of cupric chloride, and heated at a temperature of about 450°. The calculation of their results, as made by Haber (*loc. cit.*), is as follows :—

Temperature : $t = 430°$ C.
Initial gas : HCl = 8·5 per cent. ; O_2 = 91·5 per cent.
Pressure = 737 mm.
x observed = 0·83

hence

HCl oxidized = 0·83 × 8·5 = 7·05 c.c.
∴ Cl_2 produced = 3·52 c.c. ; H_2O produced = 3·52 c.c.
O_2 consumed = 1·76 c.c.

Final gas : composition in c.c. at 737 mm.

Total	Cl_2	HCl	O_2	H_2O
98·23	3·52	1·45	89·74	3·52

$$\therefore p_{O_2} = \frac{89{\cdot}74}{98{\cdot}23} \times \frac{737}{760} = 0{\cdot}888 \text{ atmo.}$$

$$p^{\frac{1}{4}}_{O_2} = 0{\cdot}968$$

$$\frac{x}{2(1-x)} = 2{\cdot}44$$

$$\therefore \frac{x}{2(1-x)} \cdot \frac{1}{p_{O_2}^{\frac{1}{4}}} = k' = 2{\cdot}51$$

A similar experiment at 480° gave $k' = 2{\cdot}0$.

The value calculated from equation (1) for $T = 480 + 273$ is $k' = 1{\cdot}73$.

Lunge and Marmier detected a considerable decomposition even at 310°, but the lowest temperature for technical working is above 400°. In addition, the rate of flow must be adjusted to give equilibrium. Initial gas mixtures containing only a little HCl were, of course, more rapidly brought to equilibrium than those containing more, and it was found that, below 480°, the equilibrium constant was abnormally low with gases rich in HCl. Above 480° this influence of velocity disappeared, so that equilibrium must then be attained rapidly. With mixtures rich in hydrochloric acid, showing an equal ratio HCl/O_2, the oxidation was greater with air than with pure oxygen. Lunge and Marmier considered that this result was not in harmony with the law of mass action, but the true explanation was given by Haber. The air mixture comes nearer to the equilibrium value on account of its lower acid content, whilst in the oxygen mixture the velocity of reaction is not high enough to transform the large quantity of hydrochloric acid into chlorine, although the increased oxygen concentration actually makes the reaction velocity higher. This is a good illustration of the necessity of making measurements with different rates of flow, and otherwise making certain that equilibrium is actually attained. Certainty on the second point can only be attained when it is shown that the same final state is reached with mixtures of HCl and O_2 as with mixtures of Cl_2 and H_2O.

As a result of these experiments, one may conclude that the equilibrium constant of the Deacon process—

$$k' = \frac{p^{\frac{1}{2}}_{Cl_2} \cdot p^{\frac{1}{2}}_{H_2O}}{p_{HCl} \cdot p^{\frac{1}{4}}_{O_2}}$$

has the value 2·0 at 480° C., when the gases are under atmospheric pressure. The calculated value is 1·73. The calculated value at 430° is 2·42, which confirms the experience that the lowest temperature compatible with attainment of equilibrium is the best.

The practical method of carrying out the Deacon process is as follows. A mixture of 1 vol. HCl and 4 vols. air is produced from the salt-cake furnace gas, and is passed by a hot Root's blower through cooling pipes and scrubbers,

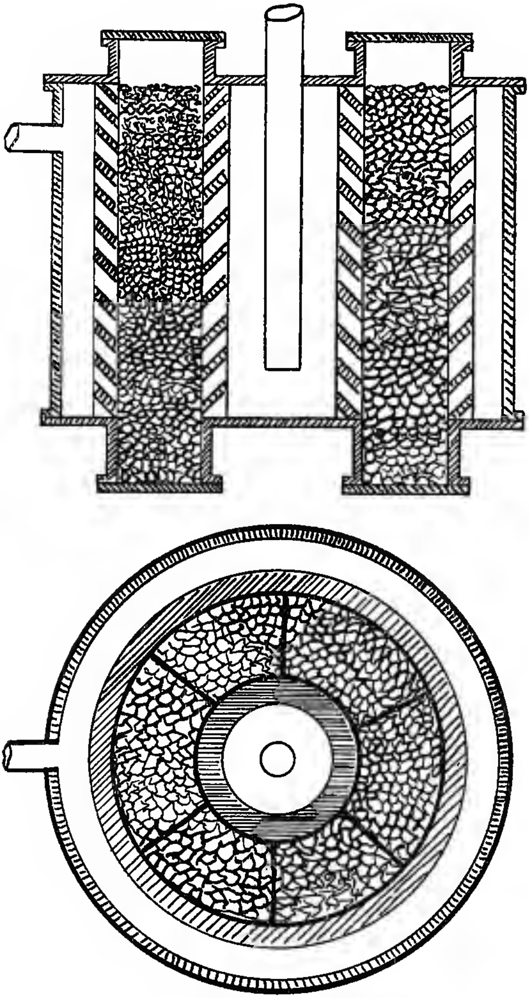

FIG. 42.—Deacon Converter.

where most of the moisture is removed. The gases are then dried in a sulphuric acid tower, and pass to a preheater, composed of 26 vertical iron pipes, 1 ft. wide and 9 ft. high, arranged in two sets in a furnace, where they are heated to 450°. The waste heat is used for heating the converters, to which the gases now pass. These (Fig. 42) are upright iron cylinders, 12–15 ft. wide, containing a ring of broken bricks dipped in a solution of cupric chloride (0·6–0·7 per cent. of copper in the mass), supported by iron shutters. The gases enter at the circumference, pass through the catalyst to the inner space, and are led off by a pipe. The annular space between the shutters is 3 ft. wide, and is divided into six compartments, one of which is emptied and refilled every fortnight. The spent catalyst is thrown away. The loss of copper is 3–4 lbs. per 1 ton bleaching powder produced.

Only two-thirds of the HCl is converted into chlorine, and the steam and unchanged HCl are condensed out in earthenware pipes and a water tower, where strong acid is recovered. The gases, containing 5 to 10 per cent. of Cl_2, are then dried in a sulphuric acid tower, and used in a special apparatus for making bleaching powder. The fuel consumption is 6–10 cwt. per ton of bleaching powder produced. The presence of H_2SO_4, SO_2, CO_2, and As_2O_3 in the hydrochloric acid is prejudicial, and these impurities must be removed. Only the "pan-acid" (cf. p. 63) can be used directly; the "roaster-acid" must be absorbed separately and sold. Hasenclever (1888) patented a process for producing a steady stream of pure hydrochloric acid gas by mixing the impure liquid acid with a little strong sulphuric acid in towers, and blowing out the HCl gas with a stream of air. The cost of re-concentrating the sulphuric acid has then to be taken into account, but the working of the Deacon process is more regular, and "roaster-acid" may then be used. This improvement of Hasenclever's has brought the Deacon process to the forefront of the successful chlorine processes.

The improved Deacon process is largely replacing the Weldon plant, as the latter wastes up to 70 per cent. of the chlorine.

The following figures (from Davis, "Chem. Eng.")

show the influence of temperature on the yield in starting up a Deacon plant :—

260°	No decomposition.
366°	5 grains Cl per cu. ft. gas.
377°	12 ,, ,, ,,
399°	17 ,, ,, ,,
420°	26 ,, ,, ,,
435°	34 ,, ,, ,,

Chlorine from Magnesium Chloride.—The loss of chlorine in the Weldon process led its inventor to look around for an improvement, and the similar loss in the ammonia-soda process also led to attempts at chlorine recovery from calcium or ammonium chloride.

The Weldon-Péchiney Process consisted in heating magnesium chloride in a current of air, and was worked for some years at Oldbury in England, and at Salindres in France. It has been abandoned, as it could not compete with the Deacon process if hydrochloric acid were used as initial substance, but it is used at the ammonia soda works at Szakowa (Galicia). The reaction involved is—

$$2MgCl_2+H_2O+\frac{1}{2}O_2=2MgO+2HCl+Cl_2$$

The process was worked as follows. A mixture of powdered MgO and Mg_2OCl_2 from a later stage of the process, made in such proportions that the evolution of heat in the neutralization is suitably reduced, is dropped into hydrochloric acid until this is neutralized. A little oxide of iron and alumina are deposited, and the liquid is run into settling tanks. The clear liquid is evaporated in an iron boiler to the composition $MgCl_2.6H_2O$, and this is run into a circular iron vessel with rotating paddles, where it is mixed with powdered magnesia until the mass solidifies, producing Mg_2OCl_2. This oxychloride, which is very hard, is broken up by letting it drop through rollers bristling with diamond points. The pieces are further dried on shelves, run on trucks through a tunnel against a current of air at 300°, when 60 per cent. of the water is removed. The lumps are then heated in special brickwork furnaces, previously heated to 1000° by large Bunsen burners, and a blast of air forced through the mass. The unchanged HCl and steam are condensed out in water, and chlorine passes on.

Of the total Cl in the mass, 6–7 per cent. comes off in the drying process, and 14 per cent. remains undecomposed. 37 per cent. comes off as HCl, and 42 per cent. as free chlorine. Less than half the chlorine is thus obtained free, but only 7 per cent. is actually lost.

In Mond's process, which was worked at Winnington in 1893, the chlorine in ammonia-soda liquors was to be utilized. The solution of NH_4Cl from which the $NaHCO_3$ had separated was crystallized and the NH_4Cl heated in an iron retort. The HCl and NH_3 gases were passed over lumps of magnesia at 350° C., which removed HCl to form the oxychloride, Mg_2OCl_2. The NH_3 passed on to the alkali process. If a neutral gas was passed through the Mg_2OCl_2, heated to 500°, and then in a current of air at 800°–1000°, chlorine was evolved—

$$Mg_2OCl_2 + \tfrac{1}{2}O_2 = 2MgO + Cl_2$$

Oxidation with Nitric Acid.—Taylor (1884) modified the process of Dunlop (1849), in which the reactions—

$$(1)\quad 3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$$
$$(2)\quad NOCl + H_2SO_4 = SO_2(NO_2)(OH) + HCl$$

alternate. A series of towers packed with ganister were used, through which HCl was passed, and down which alternately HNO_3 of sp. gr. 1·4 and H_2SO_4 trickled. The HCl was finally removed in a water tower, and the Cl_2 dried by a sulphuric acid tower. The nitrous vitriol from the towers was used in a Glover tower, or denitrated by dilution, and re-concentrated. According to Lunge, the nitric acid must be heated to 80° in order to get good results. Davis (1890) introduced air into the last of three towers down which nitric acid trickled; this was supposed to regenerate nitric acid, but residual NOCl had to be absorbed by a sulphuric acid tower—

$$(1)\quad 3HCl + HNO_3 = Cl_2 + NOCl + 2H_2O$$
$$(2)\quad NOCl + HNO_3 = N_2O_4 + HCl$$
$$(3)\quad N_2O_4 + 2HCl = N_2O_3 + H_2O + Cl_2$$
$$(4)\quad N_2O_3 + O_2 + H_2O = 2HNO_3$$

These processes are no longer worked.

Bleaching Powder.—In 1785 Berthollet proposed to use chlorine water for bleaching, and its use was started at Aberdeen in 1787, and in a works near Bolton (Lancs.) in 1788. In 1789 the so-called "Eau de Javel" was manufactured by passing chlorine into cold caustic potash solution—

$$2KOH+Cl_2=KCl+KClO+H_2O$$

The product was, however, too expensive to find much application; and it was not until 1798 when Charles Tennant proposed to use lime for the absorption that the manufacture of bleaching substances from chlorine was commercially possible. At first he used milk of lime—

$$2Ca(OH)_2+2Cl_2=CaCl_2+Ca(OCl)_2+2H_2O$$

but in 1799 he began to use dry slaked lime, and the manufacture was begun in that year at the St. Rollox works, Glasgow, the "Bleaching powder" being sold at £140 a ton. Lime had previously been used in Lancashire, and Tennant's patent was declared void. The works, however, continued to make the bleaching powder, and is still in operation. The present world's production is about 300,000 tons per annum.

The nature of the product of absorption of chlorine gas in dry calcium hydroxide has been the subject of many researches and speculations and is still not known completely. At first it was assumed to be a direct addition compound of lime and chlorine—"chloride of lime"—$CaO.Cl_2$; then Balard in 1835 suggested that it was a mixture of calcium chloride and hypochlorite in equivalent proportions, $Ca(OCl)_2.CaCl_2$, with excess of lime. The constitution at present assumed is that proposed by Odling, which is supported by the experiments of Lunge, Schäppi, and Naef, who showed that calcium chloride does not exist in the powder, but is produced by the action of water. Odling's formula is $CaOCl.Cl$.

The method of manufacture is simple in theory. The lime is produced by slaking a pure quicklime (*e.g.* Buxton lime, 98–99 per cent. CaO) by sprinkling it with water and turning over with a spade. When a fine powder is formed it is allowed to stand for ten hours to cool, and is then sieved (12–18 wires to the inch). Mechanical slakers, in which the lime is treated with water in closed vessels with agitators, are also used ; they are more rapid and create less dust than hand slaking. The powder should contain about 4 per cent. excess water and not more than 2·5 per cent. CO_2.

The slaked lime is then spread in a thin layer on the floors of chambers made of lead, 6½ ft. high, 10–20 ft. wide, and up to 100 ft. long, with a floor prepared with asphalt. Two doors with glass windows are placed at opposite ends of a chamber. The lime is raked into furrows by wooden rakes, all joints except an air hole (afterwards closed) are luted, and chlorine is admitted. The absorption, which is followed by observation of the colour of the gas through the windows, is rapid at first, but slows off, and after 12–24 hours is completed. It may be necessary to rake the lime again and rechlorinate, but when the process is finished—recognized by the absence of dust in the powder, which may be kneaded between the fingers—the excess of chlorine in the chamber is removed by blowing in a fine dust of lime by means of a hopper and fan (Brock and Minton, 1886). For 10 tons of bleach, 4 to 5 cwt. lime dust are used, which produce 6 cwt. additional bleach. The product is raked out of the chambers, and should contain at least 37 per cent. available chlorine ; up to 39 per cent. is manufactured.

With chlorine from the Deacon plant, or other dilute gas, a large number of chambers fitted with shelves, through which the gas passes on the counter-current principle, are used. They are made of flagstones, with iron pipes, and are arranged in pairs, the gas passing up one side and down the other. Eleven double chambers are arranged in series, with 16 shelves in each, on which lime is spread ½–1 in. thick. 500 sq. ft. surface are required per ton of bleach made per week.

Hasenclever's *mechanical absorbers*, consisting of several superposed lead or iron cylinders, through which lime is pushed by worm-screws or scrapers in the opposite direction to the gas, are also coming into use (Fig. 43). With strong gases, such as are produced by electrolytic processes, the chamber absorbers are generally used, as too much heat is given

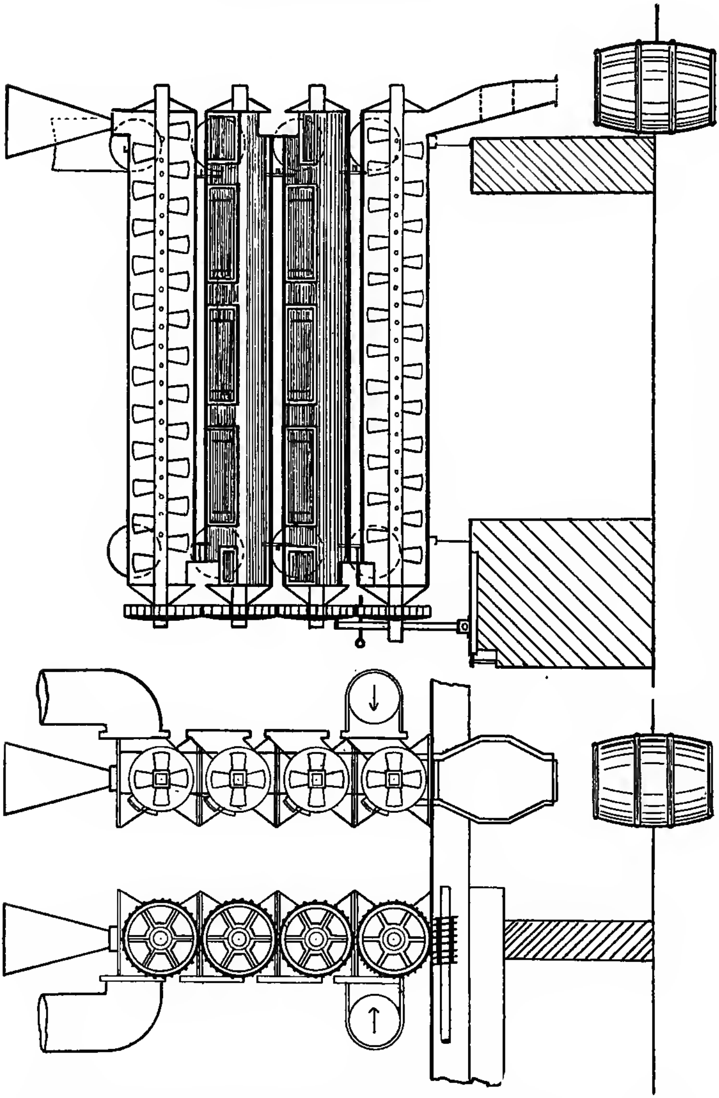

Fig. 43.—Hasenclever Bleaching Powder Apparatus.

out in mechanical absorbers, with loss of chlorine as chlorate. These gases might be diluted previous to absorption with the necessary quantity of air.

The yield of bleaching powder is 1½ times the weight of lime used, and the product is packed in hard-wood casks, or mild steel drums, with the lids not hermetically sealed. It must be stored in a cool dry place, as it is liable to decompose with evolution of oxygen—

$$2CaOCl_2 = 2CaCl_2 + O_2$$

In hot climates it is therefore best replaced by liquid chlorine in steel cylinders. The more free lime is left, the better the powder keeps; exposure to light is very deleterious.

Besides being extensively used for bleaching fabrics, chloride of lime is used as a disinfectant, especially for sterilizing water for military purposes. Three parts excess available chlorine per million destroys all coliform organisms in a polluted water after half an hour's contact.

Calcium hypochlorite, $Ca(OCl)_2$, is manufactured by the Griesheim Elektron Co., by passing chlorine into milk of lime and boiling down in vacuum. It is more stable than bleaching powder, gives a clear solution in water, and contains 80–90 per cent. available chlorine.

Sodium hypochlorite, NaOCl, is prepared in solution (5 per cent. available Cl) by precipitating bleaching powder with Na_2CO_3 or Na_2SO_4, or (in 10–15 per cent. available Cl solution) by passing chlorine through soda solution. A dilute solution is prepared by electrolyzing brine in special cells at a low temperature (not above 20° C.). These cells (Fig. 44), due to Kellner, are usually troughs with glass or porcelain partitions wound with platinum or iridium wire, which act as "bipolar" electrodes, *i.e.* alternate sides act as anodes and cathodes when the two outside electrodes are connected to the source of current. The brine is circulated through these cells from a trough underneath. About 8500 K.W.H. are required per ton available chlorine produced, and a 1–2 per cent. solution results, which is used in bleaching wood-pulp and cellulose, as a disinfectant, and in modern laundry practice with the well-known rotting effect on fabrics.

The concentration of hypochlorite reaches a limiting value, which is determined by a number of circumstances, such as the material of the anode, the current densities at the electrodes, the temperature, and the original concentration of the brine. The hypochlorite is in fact also decomposed by the current, and the limiting concentration is reached when as much is decomposed as is formed. The decomposition occurs in two ways :—

(1) Reduction by hydrogen liberated at the cathode—

$$NaOCl + H_2 = H_2O + NaCl$$

(2) Production of chlorate from the hypochlorite ion discharged at the anode in preference to the chloride ion—

$$6ClO' + 3H_2O = 2ClO_3' + 4Cl' + 6H^{\cdot} + 1\tfrac{1}{2}O_2$$

Both these effects are found to be minimized by increasing the current density, and the former is almost eliminated by adding a small quantity of potassium chromate to the electrolyte (Imhoff, 1898). The yield is also increased by keeping the solution neutral, concentrated, and cool.

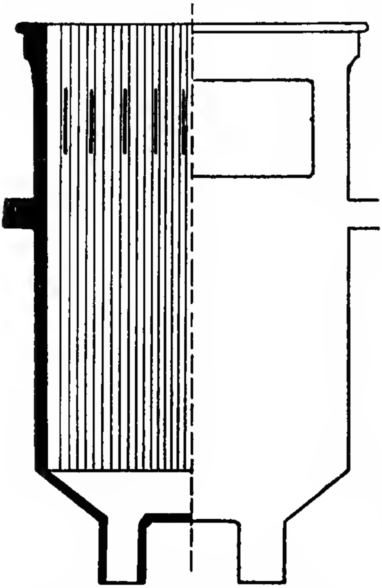

FIG. 44.—Kellner Hypochlorite Cell.

In the Haas and Oettel cell, the liquid is contained in a trough divided into compartments by partitions of carbon or other material, forming bipolar electrodes. The liquid enters each compartment below, and the gas evolved rises and carries the liquid with it out at the top through channels.

Efficient circulation is thus produced without pumps. Cells of this type are now largely used.

A mixture of NaOCl solution and boric acid is used as an antiseptic. Solid hypochlorite with 58 per cent. of water has been produced in crystals (Muspratt and Smith, 1898).

The Chlorate Industry.—In the older chlorate process, begun at St. Helens in 1847, the first product is calcium chlorate, obtained by passing chlorine into hot milk of lime—

$$6Ca(OH)_2+6Cl_2=5CaCl_2+Ca(ClO_3)_2+6H_2O$$

The first reaction, according to Lunge and Landolt (1885), is the formation of hypochlorite—

$$\text{(i)}\ \ 2Ca(OH)_2+2Cl_2=Ca(OCl)_2+CaCl_2+2H_2O$$

This is subsequently decomposed into a mixture of chlorate and chloride—

$$\text{(ii)}\ \ 3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2$$

The reaction probably occurs in two stages, with the intermediate formation of hypochlorous acid. Hypochlorous acid can in fact be produced by blowing a current of air and chlorine through a solution of bleaching powder—

$$\text{(ii}a\text{)}\ \ Ca(OCl)_2+2Cl_2+2H_2O=CaCl_2+4HClO$$
$$\text{(ii}b\text{)}\ \ 2Ca(OCl)_2+4HClO=CaCl_2+Ca(ClO_3)_2+2Cl_2+2H_2O$$

The chlorine acts as a carrier of oxygen. Heat alone without chlorine leads to much loss, as was noticed by Gay-Lussac in 1842, owing to the side reaction—

$$Ca(OCl)_2=CaCl_2+O_2$$

The milk of lime should have a specific gravity not above 16°–17° Tw.; it is contained in a cylindrical cast-iron vat (Fig. 45), 10 ft. in diameter and 5½ ft. high, with an agitating paddle and water-luted tubes. The manhole is also water-sealed. Several converters can be used, on the counter-current system. The liquid becomes warm, and froths at first when chlorine is passed through. The temperature is kept down to 60°–70°. Later on the froth disappears, and the liquid becomes pink from the formation of permanganate if Weldon chlorine is used. The run is finished in from 24 hours to 3 days, and the end-point is determined when the evolution of chlorine from the liquid on adding HCl ceases. The liquid is run into settling tanks, and may be treated so as to produce either potassium or sodium chlorates. Formerly the potassium salt alone was made directly, and the sodium salt made from it. Sodium chlorate is much more soluble than the potassium salt, and a demand for it arose in connection with the manufacture of aniline black. Péchiney first showed how to prepare sodium chlorate directly from calcium chlorate solution.

Potassium chlorate is prepared directly from the calcium chlorate solution by adding a small excess of 95 per cent. potassium chloride, and boiling down in iron pans to 70° Tw. The liquid is filtered into coolers and left several days to crystallize. The impure mass of long acicular crystals is broken up and recrystallized, when pure $KClO_3$ separates in thin plates. Some chlorate is left in the mother-liquor with $CaCl_2$, but by cooling to $-12°$, only about 1·5 per cent. is lost.

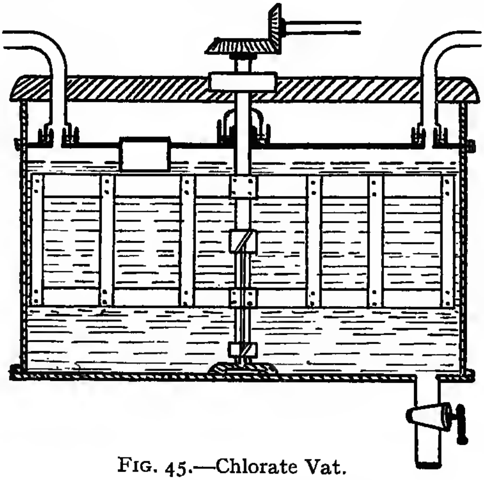

FIG. 45.—Chlorate Vat.

Sodium Chlorate.—In Péchiney's process, an "enriched liquor" is first prepared by concentrating ordinary liquor to sp. gr. 1·5 (hot), cooling to 10°–12° C., and separating the crystalline hydrate of calcium chloride in a centrifuge. Excess of sodium sulphate is then added with continuous agitation until all the Ca is thrown down as sulphate, which under proper conditions is crystalline, and can be filtered off. On evaporation most of the sodium chloride separates and can be fished out; on cooling the chlorate separates out almost pure. The mother liquor is used for the preparation of potassium chlorate.

Muspratt (1883) proposed to use magnesia instead of lime, when more chlorate is obtained, but unless the $MgCl_2$ can be utilized for making chlorine, or precipitated to recover the magnesia, the method is not so economical as the lime method, which is still largely used.

Chlorates and perchlorates are now made on a large scale by electrolysis. Solutions of chlorides are electrolyzed at 45°–100°, when the liberated chlorine at once reacts with the alkali simultaneously produced, with the formation of chlorate. This process was begun in 1890 by Ball and Montlaur in Switzerland, and is also worked in other countries where water-power is cheap. Platinum-iridium anodes and cathodes are used, placed very close together, and a current of 50–60 amps. per sq. dm. at 4·5–5 volts. The electrolyte is a 25 per cent. solution of NaCl or KCl, and the temperature is 80°. The cathode liquid is circulated round the anode, and combines with the chlorine. Imhoff (1899) found that the addition of small quantities of sodium or potassium chromates prevented the reduction of the oxy-salts by the nascent hydrogen at the cathode, and much improved the yield, which is 90 per cent. of theory. If the concentration does not fall below 10 per cent. no perchlorate is formed. The Gibbs cell was introduced in 1892 by the National Electrolytic Co. at Niagara. The largest works is that of the Corbin Chlorate Co. at Cheddes, near Mont Blanc, where 7000–10,000 H.P. water-power is used.

Perchlorates.—Perchlorates for detonators are prepared at Cheddes by electrolysis. The process is similar to that used for chlorates, but a lower current density is used, and the electrolysis is more prolonged. The chloride is first converted into chlorate, and the further oxidation to chlorate is favoured by having the solution saturated, acid at the anode, using a low temperature and a current density of 8–12 amperes per sq. dm. Ozone is evolved. The electrolysis is continued until a 75 per cent. solution of $NaClO_3$ is produced. This is then crystallized out and the chlorate electrolyzed to perchlorate. The yield is 85 per cent.

The reactions involved in the formation of perchlorates are as follows :—

(1) Discharge of chlorate ions and their reaction with water—

$$2ClO'_3+H_2O=HClO_4+HClO_2+O$$

(2) Oxidation of the chlorous acid by the oxygen—

$$HClO_2+O=HClO_3$$

The $HClO_3$ then reacts again.

The sodium perchlorate is converted into the potassium or ammonium salts by double decomposition with KCl or NH_4Cl. The dry salts are liable to detonate by friction.

Perchloric acid may be produced from the ammonium salt by dissolving it in concentrated hydrochloric acid and running the solution into warm concentrated nitric acid. Nitrogen is evolved, and on evaporation an oily liquid, $HClO_4.2H_2O$, is left.

Liquid Chlorine.—Liquid chlorine is produced for transport in steel cylinders holding about 60 kilograms, and is convenient for manufactures requiring only small amounts of chlorine or for special processes, such as the preparation of chloracetic acid for the synthesis of indigo. It is made by compressing pure dry electrolytic chlorine into cylinders by special pumps, or by refrigeration. The Badische Co. prepared over a million kilos. in 1900 for indigo synthesis, and the liquid is also used at Stassfurt for the extraction of bromine. A new use for liquid chlorine was introduced by the Germans in the attack on Ypres in the spring of 1915, when waves of "poison gas"—doubtless the accumulated stocks of the aniline dye manufacturers—were released in a vain attempt to break through the Allied line barring the road to the coast. In consequence, the manufacture of this product has now been successfully taken up in Allied countries.

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SECTION VII.—NITRIC ACID.

Nitre.—In India a considerable amount of potassium nitrate, KNO_3, is produced by the slow oxidation of nitrogenous organic matter, in the presence of bases, by atmospheric oxygen. This action occurs in the presence of the so-called nitrifying bacteria, and on the site of old villages a total of as much as 15,000–20,000 tons of nitre are produced every year by lixiviation of the soil. This source is, therefore, by no means insignificant, and may become more prominent in the near future. The discoveries of accumulations of nitre in caves add to that produced from the soil in the manner indicated. The introduction of modern sanitation and sewage disposal, already begun in India, will tend to check the production of nitre, by preventing the accumulation of refuse nitrogenous matter on the soil, and this nitrogen will be lost in the form of sewage, as is the case in most civilized countries. Even in England during the shortage of saltpetre in the Civil Wars, nitre was procured by the lixiviation of the soil of graveyards. During the isolation of France after the Revolution, the supply of saltpetre required for gunpowder ran short, and Berthollet was commissioned to investigate the possible sources of the salt. He showed how to extract it from the soil, and saltpetre works were established in great numbers to furnish the large supplies needed for the prosecution of the war. But for the investigations of this celebrated chemist, the history of France would have been very different during that momentous period. In modern times, the blockade of Germany has imposed on the chemists of that country the task of supplying the nitrates which are the staple diet of the god of war, and the problem has been solved in a manner which will be described later.

The conditions favouring the production of nitrates in the soil are a plentiful supply of readily decomposable nitrogenous organic matter, a dry climate with little rain, the presence of a mild alkali, such as the carbonates of calcium, magnesium or potassium, or decomposing felspar (either naturally present in the soil, or added to the nitre beds), and a temperature of about 37° C. The nitrates obtained on lixiviation, after a sufficient and usually considerable length of time, are those of calcium, magnesium and potassium. Potassium carbonate in the form of wood-ashes is added to precipitate the calcium and magnesium salts, and the decanted liquid is boiled down in cauldrons till it crystallizes on cooling. It is then poured off from the sediment, and allowed to stand 24 hours for the nitre to crystallize. The crude saltpetre, containing about 80 per cent. KNO_3, is refined by treating with a quantity of boiling water insufficient for complete solution, adding a little glue to precipitate the colloidal impurities, and cooling rapidly, with stirring, in wooden vats. It is dried, sifted, and packed. Potassium nitrate required for the manufacture of gunpowder is also largely made from the sodium nitrate of Chili, which is too deliquescent for use directly. Equivalent quantities of sodium nitrate and potassium chloride are dissolved in water, the potassium chloride being first dissolved to sp. gr. 1·2, and then the nitrate added to bring the specific gravity of the hot liquid to 1·5. The sodium chloride produced, being less soluble in hot water then the potassium nitrate, is deposited, and the clear liquid if allowed to cool deposits the nitre in crystals, which are washed with water and dried—

$$NaNO_3 + KCl = NaCl + KNO_3$$

Potassium nitrate is the least soluble of the four salts at low temperatures.

Another process consists in the interaction of barium chloride and sodium nitrate, and the decomposition of the barium nitrate by potassium sulphate.

Of much greater importance than potassium nitrate is the supply of sodium nitrate in the vast deposits of Chili. The zone of nitrates there appears to cover about 77,000 sq. miles, of which less than 3 per cent. is explored and prospected. In the surveyed area alone the supply is 240,300,000 tons, and this, measured at pre-war production, is stated to be sufficient for 100 years, although estimates of this important figure vary considerably ; altogether a 300 years' supply is reasonably expected.

The deposits occur in a distinct stratum of earth containing 25–50 per cent. of nitrate, called *caliche*, resting upon soft clay, and covered with a compact top layer known as the *costra*, containing less nitrate. In working, the surface soil is removed, and holes are bored in the caliche through the costra. Charges of slow-burning blasting powder are inserted and tamped, and the caliche broken into bits by the explosion. The pieces are picked out by hand and transported to the lixiviation works, called the *officina*. Here the caliche is crushed and lixiviated with boiling water. The clarified solution is run off into wooden vats and allowed to crystallize, yielding 40 per cent. of crude nitrate, and 60 per cent. mother liquors, which are used for lixiviating fresh caliche. The crystals are washed with a small quantity of water, and dried in the sun. The crude salt as exported contains 95–96 per cent. $NaNO_3$, and usually contains potassium nitrate, from traces up to 8 per cent. About 1 lb. of fuel is required in this method for 6 lbs. nitrate, but by improved processes, up to 16–19 lbs. of nitrate should be obtained per 1 lb. fuel. The extraction is performed in tanks similar to the Shanks lixiviators (p. 73), and the loss reduced from 32 per cent. in the old method, down to about 5 per cent. By this method, poorer qualities of caliche, including costra (7–16 per cent. nitrate), are workable.

The mother liquors are used to some extent for the extraction of iodine (p. 276). Caliche also contains potassium perchlorate, $KClO_4$, sometimes to the extent of 4 per cent., which, as it exerts a toxic effect on plants, is removed by allowing the crystallization to take place from the warm liquors, in which it is more soluble than sodium nitrate. The crop of crystals so obtained is practically free from perchlorate. On cooling, the two salts separate together, but when the product is treated with cold water the nitrate is dissolved; practically all the perchlorate is left in a sufficiently pure state to be used, and was shipped to Europe until the modern electrolytic methods lowered the cost so far as to make it unprofitable to export the salt. In consequence since 1901, Chili nitre has usually come into the market containing up to 3 per cent. perchlorate. If intended for agricultural purposes the nitre should therefore be tested for this salt.

The price of Chili nitre has risen about 50 per cent. during the war, but there is no doubt that the selling price could be very much reduced by competition if alternative sources, such as nitrates from the air, or from the oxidation of ammonia, are developed on a sufficiently large scale. It has been stated that the minimum cost price is only about one-third the average pre-war selling price, exclusive of duty. This is a fact which must be taken into consideration when the possibility of the economic production of nitric acid from the air or from ammonia is contemplated. By improved methods of production, financial combination, and the reduction or abolition of export duty, a rock-bottom selling price of £3 10*s*. 0*d*. per ton in Chili is predicted as a possibility.

The exports of nitre from Chili have been as follows :—

Year.	Export in tons.	Year.	Export in tons.
1830-34	16,780	1890	1,000,000
1865	491,100	1895	1,267,000
1875	334,000	1905	1,705,000
1885	512,600	1915	2,090,000

In 1904 the estimated cost of one ton Chili nitre at the works was £1 5*s*. 2*d*. to £3 15*s*. 3*d*.; in 1905 the cost in sacks delivered on board ship, including export duty, was estimated as £4 13*s*. 6*d*. to £5 17*s*. 6*d*.; in 1908 it varied from £7 8*s*. 0*d*. to £8 10*s*. 6*d*. The Nitre Syndicate in Chili was dissolved in 1909, and the price of nitre at Liverpool fell from £11 4*s*. 3*d*. in 1907 to £8 7*s*. 3*d*. in 1911. The extensive fluctuations of the price of Chili nitre, evident from these figures, make it very difficult to form an idea what effect the competition of the newer sources of combined nitrogen will have on the price of natural nitre in the future, before the impoverishment of the deposits gives a new aspect to the question. That the competition will become severer, owing to the lowering of the price of nitre, is undoubted, even if the low figure quoted above (on the authority of the Chilian Embassy in the United States) is not realized. Another complicating factor is the artificial regulation of the price of ammonia by that current for nitre, because ammonia is the most promising starting-point for the newer methods of producing nitric acid, and it will be necessary to examine closely what are the real costs of ammonia from the various sources, as contrasted with the artificial prices of the gas-works and recovery ammonia sold in competition with Chili nitre. A falling price of Chili nitre might conceivably be an advantage than otherwise to the ammonia oxidation process, because the price of ammonia would necessarily be reduced at the same time. There is reason to suppose that the average price of by-product ammonia is about five times the actual cost of production.

Less important deposits of sodium nitrate have been discovered in Colorado, Salvador, Texas, Peru, Persia, the Sahara, Egypt, and Asia Minor.

Chili nitre has two main uses—

(1) As a fertilizer, about four-fifths being so utilized under normal circumstances;

(2) As a source of nitric acid, for the manufacture of explosives, aniline dyes, and allied products, which account for the remaining one-fifth.

The so-called Nitrogen Problem arose out of two main factors—

(1) The former very large dependence of all civilized countries on the single source of supply of combined nitrogen in the Chilean nitrates;

(2) The future exhaustion of these deposits.

Attention was called to this problem by Sir William Crookes in his Presidential Address to the British Association in 1898, which has been reprinted, with additions, in a book called "The Wheat Problem" (second edition, London, 1905). The same authority pointed out that, as nitrogen exists abundantly in the free state in atmospheric air, the nitrogen problem is therefore identical with the problem of the fixation of nitrogen. The nitrogen contained in the air above 1 sq. mile of the earth's surface amounts to 20,000,000 tons. In most countries, such as Germany, France, Norway, Switzerland, and Austria, extensive research has been made during the last ten or twenty years with the object of solving the vital problem of the utilization of atmospheric nitrogen—vital in the true sense, in that the very existence of mankind is determined ultimately by the food-supply, and this in turn on the supply of fertilizers for agriculture. In the case of Germany at least, this problem has been solved with such success that it has been possible for that country to carry on the most extensive war in history, consuming prodigious amounts of nitrates for the manufacture of explosives, without the importation of a single pound of nitre from Chili. The situation of Great Britain and America is, on the contrary, extremely unsatisfactory, since both these countries, especially the former, are almost entirely dependent on the Chilian sources of supply.

The position of England with regard to synthetic nitrates is all the more surprising when it is remembered that attention was first called to the nitrogen problem by Sir William Crookes, whose experiments made in 1892, together with those of Lord Rayleigh in 1897, first indicated the possibility of the fixation of atmospheric nitrogen on a large scale. These experiments, in their turn, were based on the early work of Cavendish, who in 1781 observed the formation of nitric acid when hydrogen was burned in air, and in 1785 produced oxides of nitrogen by passing a series of electric sparks through a confined volume of air. Davy, in 1800, also produced oxides of nitrogen by passing air over a platinum wire heated by the electric current. The experimental foundations of the new industry were thus laid in this country.

In 1899 Macdougall and Howles, in Manchester, carried out the first technical experiments on the fixation of nitrogen by burning air in the electric arc, but the technical process was only realized by the work of the Norwegians, Birkeland and Eyde, in 1902, who laid the foundations of the present industry in Norway.

Nitric Acid from Nitre.—The production of nitric acid from saltpetre was known at least as early as 1250, about which time the Spanish alchemist Raymond Lully described the distillation of nitre with clay, when weak nitric acid is formed—

$$2KNO_3+SiO_2+H_2O=K_2SiO_3+2HNO_3$$

The distillation of saltpetre with sulphuric acid was carried out by Glauber (d. 1668), and nitric acid was also obtained by him on distilling alum and nitre—a process actually patented by Garroway in 1895.

Nitric acid is usually prepared in the laboratory by distilling a mixture of potassium nitrate and concentrated sulphuric acid in a glass retort, and condensing the nitric acid vapour in a cooled receiver. This is a special case of the first general method for the preparation of acids (p. 65). The interaction of potassium or sodium nitrate with sulphuric acid leads to the establishment of the state of equilibrium—

$$KNO_3+H_2SO_4\rightleftarrows KHSO_4+HNO_3$$

The product HNO_3, being the more volatile of the two acids, may be removed by distillation; the equilibrium is then disturbed, more nitric acid being produced, and ultimately practically the whole of the nitric acid is expelled.

If the distillation is carried on below 200° (nitric acid boils at 86°) the chief reaction is—

$$KNO_3+H_2SO_4=KHSO_4+HNO_3$$

or a similar reaction if sodium nitrate is used.

If, however, excess of nitre is present, and the temperature is raised to about 250°, the acid salt, $KHSO_4$ or $NaHSO_4$, reacts further with the nitrate to form the neutral salt, and another molecule of nitric acid is obtained—

$$KNO_3+KHSO_4=K_2SO_4+HNO_3$$

It is difficult, however, to push the decomposition so far in a glass retort, because the latter is usually cracked, and some nitric acid also decomposes at the higher temperature with production of red fumes of oxides of nitrogen—

$$4HNO_3=4NO_2+2H_2O+O_2$$

This reaction occurs with increase of volume, and is therefore favoured by reducing the pressure. It is, in fact, observed that at the beginning of the distillation, when air is present in the retort and the partial pressure of the nitric acid vapour is low, copious red fumes of oxides of nitrogen are evolved, but as the distillation proceeds, and the air is expelled, the colour of the vapours becomes much paler, until towards the end, when the temperature rises and red fumes again make their appearance.

All these facts are of importance in the manufacture of nitric acid, because the ordinary retort process is simply the laboratory experiment translated into chemical engineering practice. Instead of glass retorts, iron stills holding up to one or two tons of nitre are used, and the acid vapours are condensed in a suitable cooling apparatus.

According to the equations—

$$NaNO_3+H_2SO_4=NaHSO_4+HNO_3$$
$$NaNO_3+NaHSO_4=Na_2SO_4+HNO_3$$

we have by addition—

$$2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$$

The actual decomposition, however, almost certainly proceeds in two stages as described, the acid sulphate being first formed and then reacting with a second molecule of the salt of the volatile acid, as in the preparation of hydrochloric acid from salt and sulphuric acid (p. 61).

The equation—

$$\underset{170}{2NaNO_3} + \underset{98}{H_2SO_4} = \underset{142}{Na_2SO_4} + \underset{126}{2HNO_3}$$

would give the proportions—

100 parts Chili nitre (95 per cent. $NaNO_3$)
58·8 parts sulphuric acid (93 per cent. H_2SO_4).

In practice different proportions are used, because the preparation according to this equation would lead to decomposition of nitric acid with production of oxides of nitrogen which are difficult to condense and colour the acid yellow, and to the formation of a hard, difficultly-fusible residue of sodium sulphate which would have to be chipped out of the retort. To avoid decomposition of the nitric acid, and to produce the more readily fusible acid sulphate, $NaHSO_4$, known as sodium bisulphate,

(i) Weaker sulphuric acid is used, viz. 63–67 per cent., sp. gr. 1·7–1·75, usually 1·72;

(ii) An excess of sulphuric acid is used.

It is usual to add at least 20–30 per cent. excess of acid, and more is often used, so that the residue approaches the composition of the acid sulphate, $NaHSO_4$. The following proportions have been stated :—

(1) *For cylinders:* 305 nitre + 240 sulphuric acid.

(2) *For pot-retorts:*

(*a*) 250 nitre + 288 sulphuric acid (66° Bé.)
or 300 sulphuric acid (60° Bé.).

(*b*) 650 nitre (96 per cent.) + 700 sulphuric acid (sp. gr. 1·84).

The most recent practice in England appears to be to add a little more sulphuric acid than nitre by weight, viz.—

Chili nitre (95 per cent. $NaNO_3$), 1 part
Sulphuric acid (93 per cent. H_2SO), 1·08 part

for the charge. This produces, with a 98 per cent. efficiency of working, 0·726 parts of 95 per cent. nitric acid. If weaker sulphuric acid is used (cf. (1) above), about 70 per cent. nitric acid is obtained, but there is less frothing in the distillation.

In the older process the retorts were iron cylinders 5 feet long by 2 feet diameter, set in pairs in brickwork over a fire so as to get the most uniform possible heating (Figs. 46 and 47). One end was fixed, and carried the delivery pipe, and the other was removable, for introducing the charge and running off the residue. In another type the ends of the retort were closed by Yorkshire flags cemented on with a mixture of iron filings, sulphur, and vinegar. These flags had holes fitted with plugs for charging, and the fused residue was run off by a pipe. The upper part was sometimes lined with acid-resisting bricks, but the cast iron withstands the action of nitric acid vapour, and if the retort is heated so that no condensation can occur on the upper part, a lining is not necessary. Such retorts were made up to a capacity of 600 kilos of nitre; they consumed 40 kilos of coal per 100 kilos of nitre, and 15–20 hours were occupied in working through one charge. The new stills described below take up to 2 tons of nitre (2000 kilos), require only 20 kilos of coal per 100 kilos of nitre, and work off the charge in about 15 hours. The older stills are, however, in use in some of the smaller works.

Condensation of the nitric acid vapour was effected in the older apparatus by means of ten or more large stoneware Woulff's bottles, or large stoneware spiral tubes, or a combination of the two. A design of a two-still plant of the older type is shown in Fig. 47, and comprises both types of condensing apparatus. In some cases intermediate air-cooled glass tubes, 10–13 feet long, were placed between the stills and the condensing worms, the latter being immersed in cold water. These stoneware condensing worms have to be carefully made, to resist the acid and changes of temperature; those made by the firm of Doulton, of Lambeth, have long possessed a good reputation. Latterly

A, retort.
B, still-head.
C, condensing bottles.
D, condensing worm.
E, acid run-off.
F, Woulff's bottle.
G, absorption tower.
H, distributing plate.
I, lantern.
J, Woulff's bottle with lime to absorb waste gases.

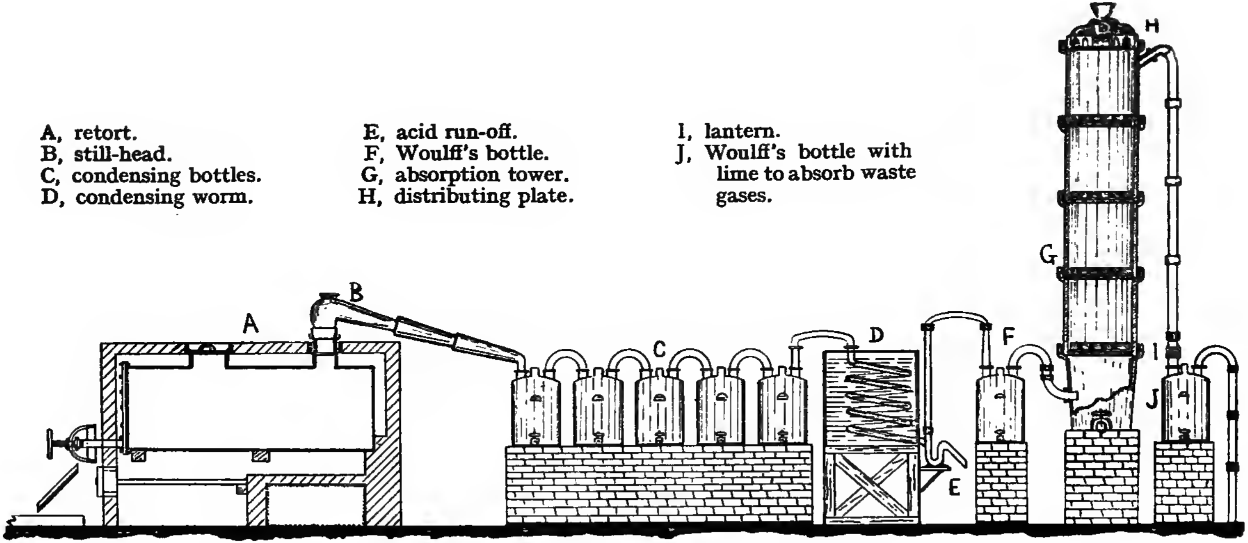

FIG. 46.—(Elevation). Nitric Acid Apparatus.

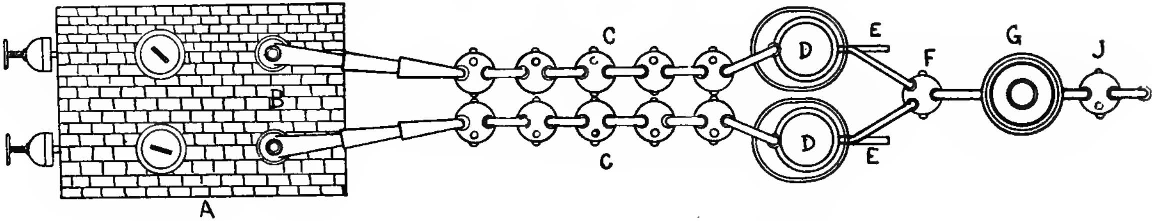

FIG. 47.—(Plan). Nitric Acid Apparatus.

they have been replaced to some extent by silica spirals, 3 inches in diameter and 30 feet long, which are less liable to crack. These cost about £30 each.

Arrangements were sometimes made by means of three-way stoneware cocks to separate the distillates at different stages of the process, which vary somewhat in strength. The last portions of the distillate are weaker than the intermediate portion, probably on account of the reaction—

$$2NaHSO_4 = Na_2S_2O_7 + H_2O$$

occurring at higher temperatures, which also causes frothing. The first portions of distillate contain the water present in the nitre.

The parts of the condensing apparatus may be luted with one of the following putties, which resist the action of nitric acid quite well :—

	II.	I.
China clay	20	20
Asbestos powder	40	40
Linseed oil	21	18
Short-fibre asbestos ..	8	8
Tallow	—	2½

The oxides of nitrogen in the exit gases are absorbed in a tower in which water circulates over hollow stoneware balls or rings. An older type of condensing tower is the Rohrmann tower, in which the gases enter at the bottom, together with sufficient air and steam to produce dilute nitric acid, which is condensed on inverted perforated stoneware jars standing on perforated shelves in the tower. The reaction is then—

$$4NO_2 + O_2 + 2H_2O = 4HNO_3$$

Working as described, with sulphuric acid of density 1·72, one obtains a nitric acid of sp. gr. 1·38–1·41. To obtain a stronger acid, sp. gr. 1·5–1·52, sulphuric acid of sp. gr. 1·85 must be used, but then frothing is liable to occur, when sulphuric acid and salts are carried over, and also oxides of nitrogen produced which colour the nitric acid yellow. This yellow colour came to be regarded as an indication of the strength of the nitric acid, since it usually appears in the preparation of the strongest acid, and an acid containing dissolved oxides of nitrogen is specially prepared, under the name of "Fuming Nitric Acid," by distilling a mixture of 100 parts of Chili nitre, 100 parts of sulphuric acid of sp. gr. 1·85, and 3·5 parts of starch. The starch reduces a portion of the nitric acid to oxides of nitrogen, N_2O_3 and N_2O_4, which dissolve in the concentrated nitric acid to form a yellow solution, which has strong oxidizing properties—the lower oxides of nitrogen acting catalytically in many reactions with nitric acid, such as the dissolving of metals. If this yellow liquid is diluted with water it turns green, and if a large amount of oxides of nirogen is present, even blue, owing to the formation of nitrous anhydride, N_2O_3, which has a deep blue colour—

$$N_2O_4+H_2O=HNO_3+HNO_2$$
$$2HNO_2=N_2O_3+H_2O$$

For many purposes, however, as in dyeing, the acid must be free from lower oxides of nitrogen, This acid is made by warming the yellow acid to 60°–80° and blowing a current of dry air through it, when the oxides of nitrogen are carried off. Hirsch (1888) allowed the acid to trickle continuously down a spiral tube, up which warm air was passed. Another, less satisfactory, method of separating oxides of nitrogen is to add to the yellow acid a little lead peroxide, PbO_2, when the oxides of nitrogen are converted into lead nitrate, which as it is insoluble in strong nitric acid separates along with the excess of lead peroxide—

$$PbO_2+N_2O_4=Pb(NO_3)_2$$

The insolubility of lead nitrate in strong nitric acid allows that acid to be passed through lead pipes; if water is admitted, however, the metal is violently attacked.

The following grades of nitric acid are made and sold :—

Trade name.	Sp. gr.	Degree Twaddel.	Percentage HNO_3.
Single aqua-fortis ..	1·420	84	70
Double aqua-fortis	1·500	100	94·1
Monohydrate ..	1·520	104	100·0

Other impurities present in the commercial acid besides oxides of nitrogen are sulphuric acid and sodium sulphate, carried over mechanically as spray from the retort, chlorine from chlorides present in the nitre, iodine from iodates, and occasionally perchloric acid from perchlorates often found in Chili nitre. The sulphuric acid is chiefly confined to the acid collecting in the first receiver, whilst chlorine collects further on in the series, usually in the third receiver, owing to the formation and decomposition of the nitrosyl chloride produced—

$$3HCl+HNO_3=NOCl+Cl_2+2H_2O$$
$$NOCl+H_2O=HNO_2+HCl$$
$$3HNO_2=HNO_3+2NO+H_2O$$
$$2NO+Cl_2=2NOCl$$

The perchloric acid comes over at the end of the distillation, as the stable hydrate, $HClO_4.2H_2O$, has a boiling-point of 200°.

Modern Nitric Acid Plants.—The improvements introduced in the manufacture of nitric acid from nitre have been in the following directions :—

(1) Improved design and increased capacity of the retorts (up to 2 tons of nitre).
(2) Condensers of increased efficiency.
(3) Working under reduced pressure.
(4) Improved methods of condensing the oxides of nitrogen in the exit-gases, or the reduction in the amount of these oxides produced.

With a modern plant the cost of production of strong nitric acid amounts to about £18 per ton, with Chili nitre at £8 per ton (cf. p. 159).

The retort or still (Fig. 48) consists of a large pot made of cast iron, or one of the acid-resisting alloys mentioned on p. 32; it is cast in two or three pieces which are clamped together with asbestos packing and built up in a brickwork furnace so as to allow of very uniform heating. At the top of the retort is a manhole for introducing the charge, and an exit pipe for the vapours of nitric acid, which is usually made of stoneware, acid-resisting metal, or silica. In this exit pipe is a "lantern," *i.e.* a stoneware box with glass windows, or else a short length of glass pipe, for the purpose of observation. As already mentioned, the retort takes up to 2 tons of nitre per charge, requires 20 kilos of coal per 100 kilos nitre, and works off the charge in 15 hours. In the latest Valentiner plants it is claimed that 5 hours are sufficient. Gas firing is also used. The proportions of nitre and sulphuric acid are the following, allowing a 30-per-cent. acidity in the nitre-cake :—

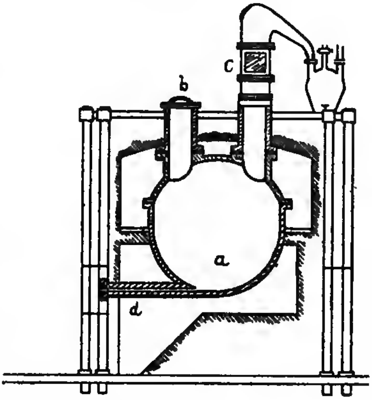

FIG. 48.—Modern Nitric Acid Retort.

a, retort; *b*, charging hole; *c*, lantern; *d*, discharge pipe.

	Nitre (95 per cent. $NaNO_3$) ..	1 ton
	Sulphuric acid (93 per cent. H_2SO_4)	1·08 tons
or	Sulphuric acid (80 per cent. H_2SO_4)	1·25 tons.

The nitre should be dried by gentle heating before use.

The weaker sulphuric acid produces a weaker nitric acid but causes less frothing. With acid not stronger than 80 per cent. H_2SO_4 there is very little frothing. Less sulphuric acid may be used, but then the residual nitre-cake is less fusible, and more difficult to remove, and the life of the retort is correspondingly reduced.

At the bottom of the retort is a run-off pipe fitted with a plug, from which the still fluid residue of acid sodium sulphate is run off after the distillation into an iron pan to form on cooling a solid sheet of nitre-cake, which is broken up with a hammer.

Processes for continuous working, by feeding in nitre and sulphuric acid, and removing the nitre-cake continuously, have also been patented, but are very little used in this country. Arrangements for heating the retorts by means of an oil-bath have also been described.

According to the arrangement used for condensing the vapours of nitric acid, there are several patented nitric acid plants, of which the following are the best known :—

(1) The Guttmann System.
(2) The Hart System.
(3) The Valentiner System.

Guttmann's Nitric Acid Plant.—In this system the vapours from the retort are mixed with sufficient air before condensation to oxidize the lower oxides of nitrogen to nitric acid in the presence of water. In view of the fact that nitric acid vapour tends to decompose with formation of oxides of nitrogen when the pressure is reduced, say by admixture with an indifferent gas, the wisdom of Guttmann's mode of procedure is not altogether clear on theoretical grounds, and the same may be said of the process of Valentiner, in which a reduced pressure is produced throughout the apparatus by means of a pump. Both processes are said to give excellent results in practice, but this may be partly due to the care which is taken to recover the oxides of nitrogen, which are certainly produced in both processes.

In Guttmann's system the vapours from the retort are mixed with air either by admitting air, preheated by passing through a tube in the furnace flue, into the delivery pipe from the retort through a narrower tube inserted into the outlet pipe, or in another arrangement by sucking air into an enlargement connected with this outlet pipe, or through perforations in the socket-pipe connecting the outlet with the condensing arrangement. The first arrangement is more under control, as the second and third depend on the suction produced by the nitric acid vapour for the admission of air.

The condensing arrangement (Fig. 49) consists of a preliminary receiver C to collect spray from the retort, and the battery D of six vertical stoneware pipes with bends above and a connecting pipe below in which the condensed liquid acid collects, and from which it runs off into the stoneware receiver E. These pipes, except the first, are immersed in a tank of water. The exit pipes from the receiver and the condenser are joined, and lead the gases containing oxides of nitrogen to the absorption tower, or set of towers, F. These are made of acid-resisting stoneware pipes, 36 in. diameter, in 3-ft. sections, to a height of about 12 ft., and are packed inside with hollow perforated stoneware balls, down which water trickles. The acid collecting at the bottom of the tower is lifted back to the top, and so circulates until it reaches a strength of about 60 per cent. HNO_3, when no further absorption occurs. This acid may be put back into the still with a new charge.

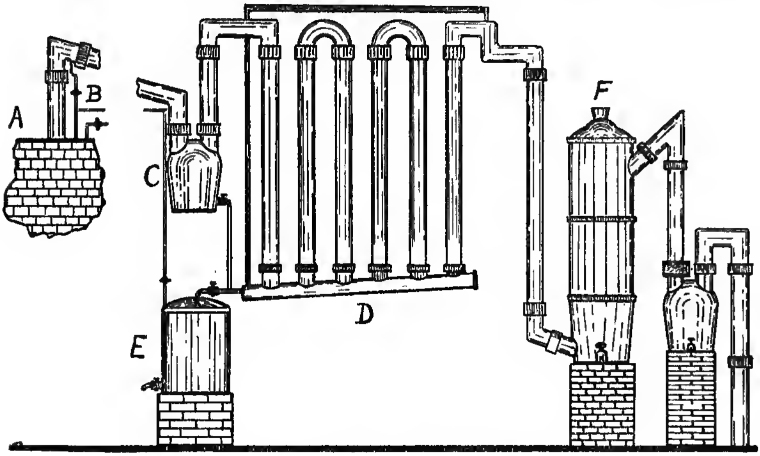

FIG. 49.—Guttmann's Nitric Acid Apparatus.

A, retort; B, air tube; C, spray catcher; D, condenser; E, collection bottle; F, absorption tower.

The reactions in the absorption towers depend on the temperature, and take place somewhat slowly, because sufficient time must be allowed for the oxidation of nitric oxide, NO, to nitrogen dioxide, NO_2, this being a somewhat slow reaction with dilute gases. With 10 per cent. by volume of nitric oxide in air a time of contact in the towers of two and a half minutes should be allowed; with 20 per cent. gas, such as is usually met with in retort plants, one minute is sufficient.

Below 50° C. the reactions in the tower are—

(1) $2NO_2+H_2O=HNO_3+HNO_2$ (rapid)
(2) $3HNO_2=HNO_3+2NO+H_2O$ (slow)
(2*a*) $HNO_2+NO_2=HNO_3+NO$ (rapid)
(3) $2NO+O_2=2NO_2$ (slow)

Above 50° practically no nitrous acid is produced, and the reactions are—

(1) $3NO_2+H_2O=2HNO_3+NO$ (rapid)
(2) $2NO+O_2=2NO_2$ (slow)

The maximum strength of acid which can be produced by the absorption of oxides of nitrogen in water in towers is about 68 per cent. HNO_3; the absorption becomes slow at about 55 per cent. strength, and the usual strength obtained is 60 per cent.

The tower packing should occupy as little space as possible (about 10–20 per cent. of the tower space). Perforated hollow stoneware balls (Guttmann balls), or stoneware rings 4 in. diameter and 4 in. high, piled up in tiers so as to break up free channels (Raschig rings), are suitable; dense packing such as flints or granite blocks is quite unsuitable, as it takes up too much space and reduces the time of contact of the gases in the tower which is required for the oxidation of the NO. Coke, slates, and brickwork packing are worse than useless for nitric acid, as they rapidly disintegrate and choke up the towers.

The loss in an efficient Guttmann plant should be less than 1 per cent.; 2 per cent. is easily attained, but 5 to 7 per cent. of the total acid is in the form of weak acid in the tower, which is recovered as strong acid in the next distillation. One ton of nitre can be worked through in 10 hours in each still, and the discharging and recharging of the retort take 2 hours. A plant of four stills costs £1450, with buildings and erection; it produces 9820 lbs. of 96·5 per cent. acid in 24 hours, requiring the labour of four men, and consuming 15 cwt. of coal.

Hart's Nitric Acid Plant.—In Hart's system the condensation is effected in horizontal glass tubes 2 metres long and 4·5 cm. diameter, connected with two wider vertical stoneware pipes, to one of which the delivery pipe from the retort is joined (Fig. 50). The pipes are cemented with a mixture of asbestos powder and water-glass. Cotton "sponge-cloths" are hung over the glass tubes and cold

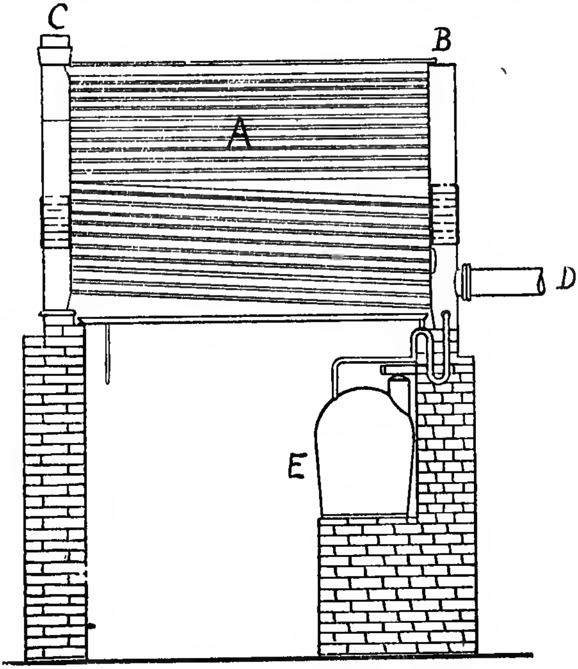

FIG. 50.—Hart's Condenser for Nitric Acid.

A, cooling tubes; B, C, upright stoneware tubes; D, delivery pipe from retort; E, receiver.

water dropped on them from above. The acid runs out at the bottom to a receiver. The cost of a plant of the same capacity as the Guttmann described above is £1200, the costs for labour and fuel being about the same. The Hart condensing plant has given very satisfactory results, and is in addition cheap and easily repaired.

Silica Condensers.—In modern plants the stoneware cooling worms are often replaced by coils of "Vitreosil," or semi-fused silica, 3 in. diameter and 30 ft. long, and complete condensing plants of silica in the form of S-pipes with flanges and sockets like stoneware pipes, are now on the market. These are set horizontally, luted with asbestos and water-glass, and are very good, although leaks at the connections are liable to develop. The vapours may pass in the same direction as the liquid acid, or in the opposite direction, when the system is called a "reflux" condensing system.

Uebel's Process.—In this process (Brit. Pat. 19881 of 1913) the whole of the sulphuric acid is put into the still, but only part of the nitre, and the distillation carried out at 140°, when the whole of the nitric acid is expelled in a very concentrated form (Phase I). The rest of the nitre is then introduced gradually, and the temperature raised to 160°–170°, when concentrated acid also comes off (Phase II). The receiver is then changed, and the temperature raised to 250°, when a weaker acid distills off. The advantages claimed for this process are the production of a very concentrated acid, the absence of crust-formation in the retorts, the absence of frothing, and an even distillation.

Production of Nitric Acid under Reduced Pressure: the Valentiner Process.—A new method of producing nitric acid from nitre was introduced by Valentiner in 1891, in which the process was carried out under reduced pressure. The still holds 1 ton of nitre, and is connected with a condensing apparatus, at the end of which is a vacuum pump with a 12-in. cylinder, having a 16-in. stroke, and working with 60 revolutions per minute. The nitric acid distils off at a temperature of about 100° under the reduced pressure of about 25 in. of mercury, and there is claimed to be less decomposition into oxides of nitrogen than in distillation under atmospheric pressure.

The vapour from the still A (Figs. 51 and 52) is passed through a preliminary cooler B, half filled with pumice to stop spray, and then to one or two silica or stoneware spirals C, connected in series or parallel and immersed in cold water. The concentrated acid (96 per cent.), which forms 80 per cent. of the distillate, is collected in the receiver *a*, and the weaker acid is collected in the receiver *b* by means of a three-way stopcock. After these receivers is a reflux condensing coil D, in which acid is condensed and runs into a receiver *c*. From this coil the vapour passes to a number of stoneware Woulff's bottles, E. The first half of these are empty and half filled with water alternately, and the second half are empty and half filled with milk of lime, alternately. These serve the purpose of the towers in the Guttmann plant, but are less efficient, so that in the newer types of Valentiner plant the bottles are replaced by towers, F. Finally the exit gases, freed from oxides of nitrogen by the milk of lime, are sucked off to the vacuum pump G, which draws in some caustic soda solution at each stroke to minimize corrosion.

The advantages of the Valentiner system are the shorter time needed for working the charge, the low fuel consumption, absence of leakage to the outside, and the high concentration of acid produced. Its disadvantages are its high capital cost, danger of frothing, and the liability of the pump to corrosion. The danger of frothing is reduced by the improvement of Valentiner and Schwarz (Germ. Pat. 144,633 of 1902), in which 95 per cent. sulphuric acid is added a little at a time, and the vapour of nitric acid washed with concentrated sulphuric acid.

The first part of the distillation is carried out at 80°; the second part (when Na_2SO_4 begins to be formed) at 120°–130°, under 650 mm. pressure, instead of 165° as in the ordinary processes. At the end, the pump is stopped

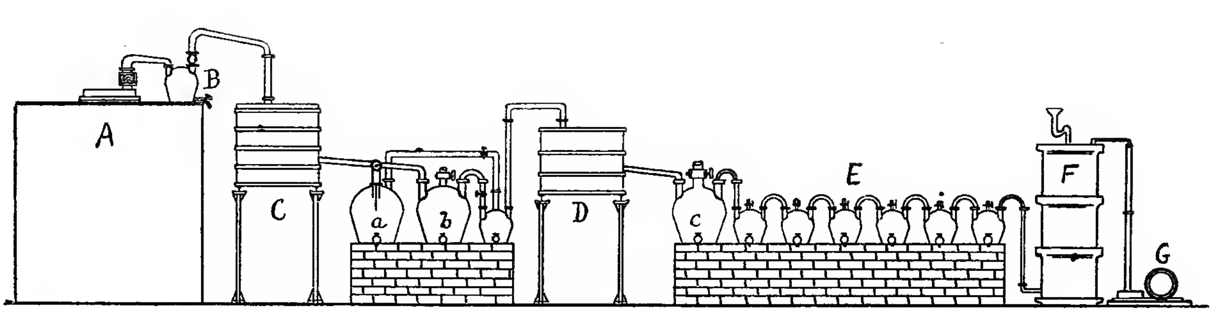

FIG. 51.—Valentiner Nitric Acid Plant (Dreyfus Pattern).

A, retort; B, spray catcher; C, cooling worms; *a*, *b*, *c*, receivers; D, cooling worm; E, Woulff's bottles; F, absorption tower; G, pump.

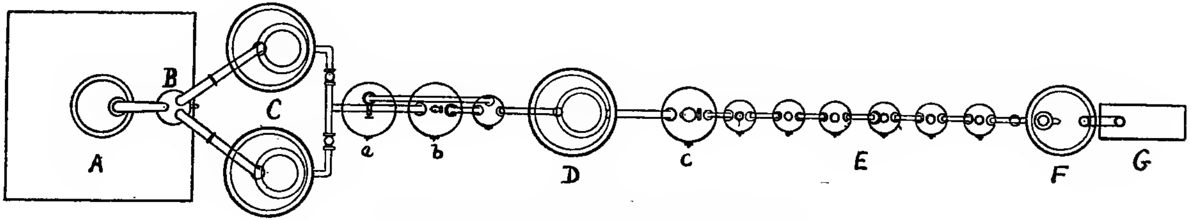

FIG. 52.—Valentiner Nitric Acid Plant (Plan).

and the temperature raised to 175° to melt the nitre cake.

Patents for the automatic charging and discharging of the retorts have apparently not proved successful in practice, as nearly all plants still work on the discontinuous system.

In Raschig's process the vacuum is maintained by long balancing columns (cf. Fig. 1), the distillation being carried out at 170°. The materials are supplied and the residues removed by long vertical pipes to give the requisite head.

Nitric acid over 90 per cent. strength may be stored in iron tanks lined with chemical lead; weaker acids should be stored in stoneware jars or glass carboys.

The Cost of Nitric Acid by the Retort Process.—The capital cost of a Guttmann plant for the production of 9820 lbs. 96·5 per cent. acid per 24 hours, inclusive of buildings and erection, but exclusive of any royalties, is £1450. It requires four men and 15 cwt. coal per 24 hours (see p. 155).

Production of acid per year (8750 hours) = 1600 tons
∴ capital cost of plant per ton 96·5 per cent. acid per annum = £0·907
∴ capital cost of plant per ton 100 per cent. HNO_3 as 96·5 per cent. acid per annum = £0·940

According to the data on p. 145, the charge in the retort is—

1 ton Chili nitre (95 per cent. $NaNO_3$)
1·08 tons sulphuric acid (93 per cent. H_2SO_4)

which, with an efficiency of 98 per cent., produces 0·726 ton nitric acid (95 per cent. HNO_3), or 0·690 ton HNO_3 (100 per cent.) in the form of 95 per cent. acid.

The material for 1 ton HNO_3 in the form of 95 per cent. acid will therefore be—

$1 \div 0·690 = 1·45$ tons Chili nitre (95 per cent.)
$1·08 \div 0·690 = 1·55$ tons sulphuric acid (93 per cent.)

The fuel per ton HNO_3 (96·5 per cent.) is $\frac{15 \times 2240}{9820 \times 20}$

$$=0·171 \text{ ton}$$

or per ton HNO_3 (100 per cent.) as 96·5 per cent. acid

$$=\frac{100 \times 0·171}{96·5}=0·177 \text{ ton}$$

The cost of fuel at 7*s*. 6*d*. per ton is therefore £0·067 per ton HNO_3. The cost of sulphuric acid (93 per cent.) may be taken as £3 per ton; that of nitre is very variable (cf. p. 140), but will be taken as £8 per ton.

The production cost of 1 ton HNO_3 as 95 per cent. acid is thus—

	£
1·45 tons Chili nitre at £8 per ton ..	11·600
1·55 tons sulphuric acid at £3 per ton ..	4·650
0·177 tons coal at 7*s*. 6*d*. per ton ..	0·067
Wages four men at 5*s*. a shift	0·228
Amortization on £0·94 at 10 per cent. ..	0·094
General expenses, stores, etc.	1·500
Total	£18·140

Cost per lb. HNO_3 as 95 per cent. acid=1·943*d*.

The corresponding costs with Chili nitre at other prices can readily be found; thus with nitre at £5 and £10 per ton, respectively, the costs of production of the nitric acid will be £13·8 and £21·04 per ton, respectively.

From these figures, however, must be deducted the value of the nitre-cake remaining in the retorts after the distillation. This can be used for various purposes, which are described in the next section, and has therefore a commercial value. It is usually applied in the works to the preparation of salt-cake (Na_2SO_4) to replace a certain amount of sulphuric acid.

Utilization of Nitre Cake.—Although the nitre cake, or acid sodium sulphate, $NaHSO_4$, obtained as a by-product in the manufacture of nitric acid by the retort process has long been utilized in the works by adding it to the charge in the salt-cake furnace in place of part of the sulphuric acid, the present shortage of sulphuric acid has led to several new uses being found for nitre-cake. This is especially necessary, as in modern practice a much larger amount of "free acid" (as $NaHSO_4$) is present in the cake than was formerly the case.

In 1915 an enquiry was instituted by the Society of Chemical Industry, which resulted in a number of suggestions for the utilization of nitre-cake (*J.S.C.I.*, **35**, 857, 1916; *Chem. Trade Journ.*, 1916, 28, 109, 393). Nitre-cake may be used in many cases as a substitute for sulphuric acid :—

(1) In the salt-cake process, in which a mixture of salt and nitre-cake is roasted, with production of salt-cake and hydrochloric acid—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl$$

(2) In the preparation of superphosphate.
(3) In the extraction of copper from pyrites cinder.
(4) In the extraction of zinc by roasting blende with nitre-cake, also for roasting copper and nickel ores, together with common salt.
(5) In the preparation of sodium alum.
(6) Roasting with felspar or clay, with production of alum, or potassium sulphate.
(7) In opening up tungsten ores by fusion.
(8) For converting sodium chromate into sodium dichromate, and sodium manganate into sodium permanganate.
(9) For absorbing ammonia in the production of sulphate, 10 per cent. of the acid may be replaced by nitre-cake, the product containing 23–24 per cent. NH_3 (*Gas Journ.*, 1916, p. 74). It may also be used for the production of ammonium sulphate by heating with leather clippings, and to prevent the escape of ammonia from manure heaps.
(10) In the preparation of Epsom salts from magnesite.
(11) In the preparation of "permanent white," $BaSO_4$.

(12) In decomposing lime soaps of fatty acids, or soapsuds.

(13) In decomposing the sodium sulphite residues from phenol manufacture, with production of SO_2.

Special uses are—

(14) In textile industries for extracting grease from wool, etc., by means of a hot aqueous solution of nitre-cake.

(15) In sizing paper, where 20 per cent. of the aluminium sulphate may be replaced by nitre-cake.

(16) In making and glazing slag bricks.

It has been proposed to recover sulphuric acid from nitre-cake as follows :—

(17) Roasting with iron scales (Fe_3O_4).

(18) Fusing with sand or molten slag, when sodium silicate is produced, and SO_2 liberated.

(19) Blowing steam and air into the fused nitre-cake.

(20) Neutralizing the free acid with soda, or by roasting with salt, then reducing by fusion with carbon, when sodium sulphide, Na_2S, is formed. This may be decomposed by CO_2, with formation of H_2S, and the latter converted into sulphur by the Claus process. The Na_2S could also be roasted with limestone, as in the black-ash process, and the sulphur recovered from the alkali waste in the usual way. Sodium carbonate is produced in both cases.

Modern Processes for the Manufacture of Nitric Acid.—The nitrogen problem will receive a complete solution when nitrates, or ammonia, can be prepared economically and on a sufficiently large scale from atmospheric air. A partial solution of the problem is the conversion of ammonia, which is obtained in fairly large quantities as a by-product in the manufacture of coal-gas and of coke, into nitric acid by oxidation. Both the complete and partial solutions of the nitrogen problem have gone a fair way to completion, as far as a knowledge of the methods goes, during the last ten years. The following summary shows the main lines in which technical application of the results of chemical research has been made :—

(1) The direct combination of oxygen and nitrogen in atmospheric air at high temperatures in the electric arc, followed by oxidation of the nitric oxide, NO, so produced to nitric acid—the Arc Process.

(2) The absorption of atmospheric nitrogen by calcium carbide or aluminium carbide, with production of calcium cyanamide, $CaCN_2$, or aluminium nitride, AlN, from which ammonia is obtained by treatment with water, and this ammonia is then oxidized to nitric acid—the Cyanamide and Serpek Processes.

(3) The combination of atmospheric nitrogen with hydrogen to produce ammonia, followed by the oxidation of the ammonia—the Haber Process.

(4) The oxidation of by-product ammonia to nitric acid.

The first process will be considered in this section, and the remaining processes, in so far as they concern the Alkali Industry, in the following sections.

The Arc Process.—A detailed description of the arc process does not properly belong to this volume, but a few remarks on the main outlines of the method must be made in order that the other processes may be properly understood.

The production of nitric acid by the action of electrical discharges in air in the presence of water or alkalies, which was discovered by Cavendish in 1785, is a process which is executed in nature on a vast scale. By the action of electrical discharges in the atmosphere, no less than 250,000 tons of nitric acid are washed down to the soil by rain in a period of 24 hours. If only one per cent. of this nitric acid could be collected, the nitrogen problem would be disposed of for many generations. This, however, is impossible, and attempts have therefore been made to reproduce the natural conditions by submitting air to electrical discharges in such a manner that the products of the action can be collected. Since it has been shown that the main action of the electrical discharge, if not the sole action, is produced by the high temperature, it is evident that the most efficient form of discharge is the arc, in which the highest temperatures are produced in the smallest possible space.

The chemical reactions involved are the following :—

(1) The synthesis of nitric oxide in the arc at high temperatures—

$$N_2+O_2 \rightleftarrows 2NO$$

(2) The secondary oxidation of the nitric oxide when the gases from the arc cool down to 600°, this reaction only reaching completion at about 130°, and even then proceeding somewhat slowly, especially in the dilute gases obtained from the arc furnace—

$$2NO+O_2 \rightleftarrows 2NO_2 \rightleftarrows N_2O_4$$

(3) The interaction of the nitrogen dioxide with water to produce ultimately nitric acid—

$$2NO_2+H_2O=HNO_3+HNO_2$$
$$3HNO_2 \rightleftarrows HNO_3+2NO+H_2O$$

The equilibrium yields of nitric oxide from air at various temperatures in the arc are as follows :—

Temperature (absolute).	Per cent. Nitrogen.	Per cent. Oxygen.	Per cent. Nitric Oxide.
1811	78·92	20·72	0·37
1877	78·89	20·69	0·42
2033	78·78	20·58	0·64
2195	78·61	20·42	0·97
2580	78·08	19·88	2·05
2675	77·98	19·78	2·23
3200	76·6	18·4	5·0

The percentage of nitric oxide in the gas from the arc furnace does not, in the best working, exceed about 2 per cent. by volume, although the equilibrium percentage at 3000° is already 5, and the temperature of the arc is higher than this. The lower yield is explained in two ways. In the first place, only a fraction of the air passing through the furnace actually passes through the arc and attains the high temperature; and secondly, some of the nitric oxide produced, which is an endothermic compound, and consequently less stable at lower temperatures, breaks up again on leaving the arc. The yield obtainable for a given expenditure of energy in the arc will therefore depend on the extent to which decomposition of nitric oxide produced at the arc temperature can be prevented by rapid cooling, for below a certain temperature the rate of decomposition of nitric oxide is exceedingly small, although the compound is still unstable. The additional air no doubt serves very materially in promoting this cooling. The experiments of Jellinek have shown that the rate of decomposition of nitric oxide becomes so slow at temperatures below 1200° C. as to be negligible in practice.

In Table I the times for the attainment of half the equilibrium concentrations of NO in air at various temperatures are given. In Table II the times for dissociation of pure NO to the extent of one-half are stated. It will be seen that above 2300° C. the rate of combination is practically instantaneous; it is 10,000,000 times quicker at 3000° than at 1900°. The rate of decomposition is seen to be slow below 1200°.

TABLE I.

Temperature Centigrade.	Time required to produce half the equilibrium concentration of NO in air at atmospheric pressure.
727	81 years.
1227	30 hours.
1427	1 hour.
1627	2 minutes.
1827	5 seconds.
2027	0·2 second.
2227	0·01 second.
2627	0·00003 second.

TABLE II.

Temperature Centigrade.	Time for half decomposition of pure NO into oxygen and nitrogen at atmospheric pressure.
627	123 hours.
827	10 hours.
1027	44 minutes.
1227	3 minutes.
1427	15 seconds.
1627	1 second.
1827	0·07 second.
2027	0·005 second.

The aim of the inventor has therefore been to produce as high a temperature (at least 3000°) in the arc as possible, and to cool the products of reaction with all possible speed below 1200°. Various types of furnace have been devised; the following are in actual operation.

(1) *The Birkeland and Eyde Furnace*, patented in 1902, and extensively used in Norway. The air is blown or sucked through a circular flat arc flame, produced by deflecting the arcs struck across water-cooled electrodes, by means of a powerful electromagnet. Each furnace of the modern type utilizes 3000 kw. The temperature of the arc is about 3500° C., and the gases escape at about 1000° from the furnace, containing 1·25 to 1·5 per cent. NO by volume. About 2·1 cu. metres of air are passed through the furnace per K.W.H. applied at the arc, and 90 per cent. of the heat generated in the arc appears in the escaping gases, and is used to raise steam, perform evaporation, etc. About 70·6 grams of nitric acid, HNO_3, are produced by the expenditure of 1 K.W.H.

After cooling somewhat, the gases are passed through Babcock-Willcox tubular boilers, where steam is raised, and the temperature of the gases reduced to 250°. If the whole of the steam raised were converted into electrical energy in turbo-generators, with a 20-per-cent. efficiency of heat conversion, 13 per cent. of the energy supplied to the arc could be recovered. The gases now pass through aluminium pipes to reduce the temperature to about 50°, when they enter a large tower of iron plates lined with acid-resisting material, where oxidation occurs—

$$2NO + O_2 = 2NO_2$$

This reaction, as already mentioned, requires time; in air containing 2 per cent. of NO by volume, 50 per cent. is oxidized to NO_2 in 12 seconds, 90 per cent. only in about 2 minutes.

The gases are now driven by powerful aluminium fans to the decagonal absorption towers, built of Norwegian granite slabs, each 10 in. thick, clamped together by iron bands, with asbestos and water-glass joints, into towers 65–80 ft. high and 20 ft. diameter. These towers are filled with broken quartz, and have the usual lifts for circulating water. Three such towers are connected by aluminium pipes to form the absorption system, and the acid produced by absorption is circulated until it reaches a concentration of 30 per cent., the weaker acid from the second and third towers being passed on gradually to the first tower, from which the stronger acid is withdrawn. Only about 80–85 per cent. of the oxides of nitrogen are recovered as nitric acid in these towers; the very attenuated gases from the third tower are passed through a wooden or sheet-iron tower down which falls a spray of sodium carbonate solution, a further 15 per cent. of oxides of nitrogen being recovered in the form of sodium nitrite, $NaNO_2$, of which 5000 tons per annum are used in Germany for the manufacture of dyes. The remaining 2 per cent. of oxides are emitted as waste.

The rapid growth of the industry in Norway, where almost unique opportunities for utilizing water-power presented themselves, is shown by the following table, giving the expenditure of power in the years since the first experiments were made :—

Year.	Horse-power expended.
1902	3
1903	150
1904	1,000
1905	2,500
1907	40,000
1911	55,000
1916	350,000

(2) *The Schönherr Furnace,* introduced by the Badische firm into Norway in 1905, employs a steady, noiseless arc, about 23 ft. long, burning in a vertical tube. Air circulates round this in a helical spiral, and after passing through the arc is cooled by striking against the top of the water-cooled iron outer jacket. From 1·9 to 2·1 cu. metres of air are passed through per K.W.H., and the gases contain from 1·5 to 1·75 per cent. by volume of NO. The yield of HNO_3 per K.W.H. at the switchboard has been variously stated; it probably amounts to about 75 grams. The further treatment of the oxides of nitrogen is the same as

in the Birkeland and Eyde process. At Rjukan, in Norway, Schönherr furnaces taking 1000 H.P. are used as well as the Birkeland-Eyde furnaces.

(3) *The Pauling Furnace*, experiments with which began in 1906, and led to the erection of a works at Innsbruck in 1909, has horn-shaped electrodes, the arc being blown from the narrow space between the electrodes at the bottom where it is struck, to the diverging upper ends by means of a blast of air. About 1·6 (in the newer types probably 2) cu. metres of air are passed through per K.W.H.; the issuing gases contain about 1·5 per cent. NO by volume, and thus the yield of HNO_3 per K.W.H. at the switchboard is 75 grams.

The Pauling works at Innsbruck uses 15,000 H.P., those in Italy and France 10,000 and 15,000 H.P. respectively.

It is stated that Germany has laid down plant during the war for the production of 10,000 tons HNO_3 per annum by arc processes—probably the Schönherr process.

The possibility of introducing the arc process into this country, where water-power is very limited, has also been discussed. It is suggested that electrical power from large generating stations run on the most economical lines with a high load-factor, *i.e.* the bulk of the energy being continuously used, or else applied to the arc process during off-peak periods (see below), say during the night, when other consumers are taking little or no power, might be sufficiently cheap to make the arc process a success. It may be observed that the cheapest pre-war electrical power, generated by steam or gas, cost about 0·25*d.* per unit, which is much too expensive for the arc process. Cheaper power from producer-gas plants might solve the problem, but it is evident that no ordinary power generation on the old lines can hope to succeed.

According to Landis, the price of electrical energy in America is very nearly the same whether it is derived from water power or steam, but this price evidently bears no relation to the true cost of production.

Statistics of the turbo-generator plant (18,500 K.W.) at Worcester, Mass., give 2·77 lbs. bituminous coal per K.W.H.

The cost per K.W.H. for labour is 0·056*d.* and of fuel at 17*s.* 7*d.* per ton is 0·265*d.*, making the total cost of production 0·321*d.* The costs of labour and fuel are high compared with British practice, and if the labour cost is reduced 25 per cent., and the cost of fuel put at 10*s.* per ton, the cost per K.W.H. with this plant would be 0·192*d.*, which is appreciably less than the figure of 0·25*d.* quoted above. (1 ton average coal is equivalent to 0·0925 K.W. year.)

According to Bakeland, power from coal at 5*s.* 1½*d.* per ton would work out cheaper than from water-power, and this price was quite possible in England at the pit-head.

The following table gives the estimated costs of electrical power from various sources, on a pre-war basis; it enables many interesting calculations to be made, as will be seen later.

Table of Costs of Electric Power from Various Sources.

Description of Sources of Electric Power.	Price per H.P. year (8750 hrs.) in shillings.	Price per K.W. year (=1·359 H.P. year) in shillings.	Price per K.W.H. in pence.
1. Odda, Norway; 16,800 K.W., water power ..	8·05–8·25	10·94–11·21	0·01498–0·01542
2. Svaelgfos, Norway; 40,000 H.P., water power	8·25	11·21	0·01542
3. Saulte Ste. Marie, U.S.A., water power	10·26	13·93	0·01913
3*a*. Saulte Ste. Marie, price to consumers	40·075	54·5	0·0748
4. Notodden, Norway, 40,000 H.P., water power from Svaelgfos	13·281	18·07	0·0248
5. Rossi Works, Legnano, nr. Milan, 10,000 H.P., water power	15·27	20·078	0·02755
6. La Roche de Rame, nr. Briançon, 25,000 H.P., water power	13·37	18·2	0·025
7. Chedde, Savoy, water power	18·33	24·90	0·03418
8. Swedish water power, various	13·0–49·3	17·70–67·0	0·0245–0·092
9. Cameron rapids, Ontario, water power	30·362	41·25	0·0566
10. Piano d'Orte, Italy, water power	29·4	40·0	0·0549
11. Turin Power Co., Italy, water power	40·0	54·36	0·0745

Description of Sources of Electric Power.	Price per H.P. year (8750 hrs.) in shillings.	Price per K.W. year (=1·359 H.P. year) in shillings.	Price per K.W.H. in pence.
12. Niagara, water power (price to large consumers)	49·32–83·0	67·10–112·7	0·0921–0·155
12*a*. Niagara, Ontario Power Co.	40·125	54·6	0·0749
12*b*. Niagara, delivered at Toronto	50·387	68·5	0·0940
13. American water power, various	26·15–76·8	35·6–104·5	0·0489–0·1433
14. Northern California Power Co., water power ..	50·196	68·2	0·0935
15. Power Co., Rome, water power	60·0	81·6	0·112
16. Hora-Hora Rapids, N.Z., water power	60·0	81·6	0·112
17. Montreal, water power, to consumers	60·125	81·7	0·112
18. Hull, Ottawa, water power, to consumers	62·74	85·3	0·117
19. North Wales Elect. Power & Tract. Co., Llyn Llydaw Falls, Snowdon, 6000 K.W.	470–803	638–1093	0·875–1·5
20. Blast furnace gas, with 95 per cent. load factor, England (see note) ..	34·25–41·83	46·7–56·8	0·0642–0·0780
20*a*. Blast furnace gas, America, 130 B.T.U. gas, with largest type engines	94·30	128·3	0·176
21. Producer gas, from coal (see note), England ..	41·75–63·58	56·7–86·5	0·0778–0·1187
21*a*. Producer gas, from coal, America, 600 K.W. units	202	275	0·378
22. Producer gas, from peat, Portadown, Ireland (cost of gas alone) ..	33·5	45·5	0·0625
22*a*. Producer gas from peat, cost of power	45·6	62·0	0·085
23. Oil engines, America, 160 K.W. units	242·5	330	0·453
24. From steam or gas power, England (average pre-war for large plants) ..	133·8	182·0	0·25
24*a*. From steam power, England (see note) ..	98·6–145·5	134–198·3	0·184–0·272
24*b*. Average steam engine, England	255·0	346·5	0·475
24*c*. Estimated cost at Pittsburg, U.S.A., steam power, 25,000 K.W., coal at 5*s*. 3*d*. per ton (see note)	76·0–107·0	91·1–145·8	0·125–0·20

Description of Sources of Electric Power.	Price per H.P. year (8750 hrs.) in shillings.	Price per K.W. year (=1·359 H.P. year) in shillings.	Price per K.W.H. in pence.
25. Louisenthal Power Station, 3 steam-turbo generators, 3000 K.W. each	183·80	260·5	0·357
25*a*. Louisenthal Power, estimated cost, if situated at coal-mine	127·50	173·5	0·238
26. Newcastle-on-Tyne Electric Power Supply Co., 50,000 K.W. steam-turbo generators ..	401·5–803·0	456·5–1093	0·75–1·5
26*a*. Newcastle-on-Tyne Electric Power Supply Co., cost of production ..	300	408	0·56–1·05
27. Lancashire Electric Power Co., Radcliffe, steam 8000 K.W.	284·0–327·0	386·0–445·0	0·53–0·61
28. S. Wales Electric Power Distribution Co., 7520 K.W.	225–284	306·3–386·0	0·35–0·53

NOTES ON THE TABLE.—In connection with this table, the following considerations may be noted. In the first place, the cost of power from any source is governed by two main factors, the *capital costs*, including interest, amortization, ground-rent, etc., and the *works costs*, including the cost of fuel, labour, repairs, etc. These two items vary considerably with the type of power used, the locality, the size of the plant, and the cost of labour. Very often the works cost is low whilst the capital cost is high, as with water power; in other cases the reverse is more nearly true, as with steam power, when the works cost is high. In some water power centres, as at Notodden, the works cost is so low that it hardly amounts to the interest on a steam power plant. Another consideration is the *load-factor*, *i.e.* the ratio of the average power consumption to the maximum consumption. In the case of ordinary power companies supplying power for lighting or traction the load-factor is usually less than 50 per cent., whereas in the case of continuous electrical processes, such as the arc process or electrolysis, the load factor may reach 95 per cent.

The higher the load-factor the more economical is the power, and it has been proposed to utilize power from ordinary generating stations during the periods when ordinary supply, *e.g.* for lighting or traction or works closed down during the night, is practically non-existent—the so-called "Off-peak" periods.

The price of water power, it will be observed, varies very much, from about 8*s*. per H.P. year at Odda to 60*s*.–83*s*. per H.P. year at Niagara. In the latter case it approaches the cost of steam power. The high figures, however, represent the prices charged to the consumers, and no information is given as to the actual cost of the power. There is no doubt that large profits are made, and in the case of Niagara, at any rate, the cost of the power is probably very much less than the price charged. It is often stated that England must compare unfavourably in this respect, since water power can never become highly developed, but this is a mistake, because the abundant supply of good coal, and the nearness of the industrial centres, place this country in a very favourable position. There is no doubt that with centralized power generation on a large scale, with full utilization of all sources of fuel besides the highest grade coal, and recovery of the by-products when possible, power could be obtained in England at a cheaper rate than elsewhere, with the exception of the water power of Norway and the Alps, where the conditions are unique.

Table, No. 20.—Cost per H.P. year from large power station using blast-furnace gas in England (Thwaite, *Journ. Iron and Steel Inst.*, 1907, p. 190) is 50·196 shillings plus cost of gas. A blast-furnace making 400 tons pig-iron per 24 hours develops sufficient gas for 10,000 H.P. in addition to the gas required for heating the blast and running the blowing engine.

Table, No. 21.—Costs of production of electric power with producer gas from coal, with recovery of by-products (J. J. Robinson, *Mech. Eng.*, 3rd April, 1908) per H.P. year.

Coal per ton.			Life of plant assumed.
6*s.*	7*s.* 6*d.*	8*s.*	
£2·0875	£2·422	£2·754	20 years.
£2·30	£2·634	£2·996	15 years.
£2·513	£2·846	£3·179	10 years.

These figures appear too low.

Table, No. 24*a.*—Costs of production of electric power per K.W. from steam (R. S. Hutton, *Engineering*, 7th December, 1906).

CAPITAL CHARGES.

10 per cent. depreciation on £15 per K.W.	0·042*d.*
5 per cent. interest on £15 per K.W.	0·021*d.*

WORKS COSTS PER K.W.

Locality.	Coal per ton.	Coal.	Wages.	Water, oil, stores.	Repairs.	Total.
Newcastle	5*s.* 6*d.*	0·078*d.*	0·022*d.*	0·004*d.*	0·016*d.*	0·120*d.*
Sheffield	5*s.* 8*d.*	0·096*d.*	0·072*d.*	0·003*d.*	0·038*d.*	0·209*d.*
Linwood	8*s.* 0*d.*	0·148*d.*	0·022*d.*	0·013*d.*	0·022*d.*	0·205*d.*

Table, No. 24*c.*—Costs per K.W.H. of electric power from steam, estimated by Sykes (*Tr. Amer. Electrochem. Soc.*, **27**, 409, 1915) for 25,000 K.W. station at Pittsburg with 5000–6000 K.W. generators; works costs only. Coal at 5*s.* 3*d.* per ton.

80 per cent. load-factor	0·125*d.*
60 per cent. load-factor	0·150*d.*
40 per cent. load-factor	0·200*d.*

These figures show the influence of the load-factor on the price of the power, already referred to. With a capital charge of 0·063*d.* per K.W., as given by Hutton (see above), the total cost would be 0·188*d.*–0·263*d.* per K.W.H., which is of the order of the figure 0·25*d.* quoted under No. 24 in the table. It may be remarked that fuel and labour costs are usually higher in American than in British practice, the former for the reason that the coal has usually to be transported considerable distances from the pits to the works.

The Haüsser Process.—The fact that oxides of nitrogen are produced by the explosion of a mixture of hydrogen and atmospheric air enriched with oxygen was known to Cavendish, but was investigated by Bunsen, and is described in his book on gas analysis. The following table is calculated from his results :—

Volume of detonating gas, $2H_2+O_2$, per 100 c.c. of air.	Residual air c.c. after absorption of oxides of N.	Per cent. NO produced in the explosion.	Calculated temperature of explosion.
64·31 c.c.	99·90 c.c.	0·07	2200 C.
78·76 c.c.	99·43 c.c.	0·38	2500 C.
97·84 c.c.	96·92 c.c.	2·05	2700 C.
226·04 c.c.	88·56 c.c.	7·63	3200 C.

Quite recently the production of oxides of nitrogen by the high temperatures generated in the explosion of combustible gases in presence of air has been proposed as a technical method for the preparation of nitric acid.

The heats of combustion of a molecular weight in grams of the various combustible gases and vapours which might be used for this purpose, all the products remaining in the gaseous state, are given below in kilogram-calories. They give the relative numbers for equal volumes (22·4 litres) of the substances.

Substance.	Formula.	Molecular weight.	Heat of combustion.
Hydrogen	H_2	2	58
Carbon monoxide ..	CO	28	68
Methane	CH_4	16	194
Ethane	C_2H_6	30	345
Ethylene	C_2H_4	28	316
Acetylene	C_2H_2	26	301
Benzene	C_6H_6	78	750

It will be seen that the hydrocarbons, such as occur in illuminating gas, evolve much more heat for equal volumes than hydrogen or carbon monoxide, which are the chief constituents of producer-gas and blue water-gas.

Haüsser, in his attempt to apply this observation to the production of nitric acid, introduces a mixture of air, with or without the addition of oxygen, under pressure into an explosion vessel. The mixture is exploded by a spark, and some nitric oxide is produced at the high temperature. Immediately after the explosion the hot gases escape through an exhaust valve, and the resulting cooling prevents the dissociation of the NO produced, which is then converted in the usual way into NO_2, and finally nitric acid. In short, the process consists in working a gas engine in such a way as to produce a maximum percentage of NO in the exhaust gases. About 5·56 grams of nitrogen are fixed per K.W.H., which is considerably less than the yield in the arc process, although it is said that the yield has been improved, and in any case the plant is much cheaper than the arc furnace arrangement.

In the later developments of the process, which is still in the experimental stages, the mixture of gas and air, say a mixture of 14·5 per cent. by volume of coal gas with air enriched with oxygen, is compressed into a steel bomb, the air being first preheated. The inlet valves are then closed and the mixture fired by a spark. Immediately after the explosion the gases are let out through a release valve, passing through a cooling coil and a shock-absorber to the absorption towers. Scavenging air is then admitted to sweep out the residual gas, the exhaust valve is closed, and the cycle recommences. With gas of a calorific value of 4300 Cal. per cu. metre the exhaust gas contains 0·7 per cent. by volume of NO. By means of the following improvements it is stated that this yield may be raised to over 5 per cent. of NO :—

(1) Higher compression.
(2) Preheating the air.
(3) Improved cooling of the exhaust gases.
(4) Good scavenging of the explosion chamber.
(5) Enrichment of the air with oxygen.

For a plant producing 3500 tons of 94 per cent. nitric acid per 350 working days of 24 hours, the cost per ton of acid is estimated to be £11 13*s.* 0*d.*; with English coke-oven gas, allowing the original claim of 5·56 grams nitrogen fixed per K.W.H. equivalent calorific value of the gas, it can be shown from the data in the table of costs that this figure would be raised to £15; if the new claims as to the yield were substantiated, the cost would be about £12 10*s.* 0*d.*

It may be at once stated, however, that the concentration of over 5 per cent. of NO claimed by Haüsser for his improved process, and in the other processes to be described immediately, corresponds with an equilibrium temperature of about 3000° C. It is known with some certainty that the explosion temperature for acetylene and oxygen, which is the hottest known, does not amount to more than 3500–4000° C., and in the case of ordinary illuminating gas the temperature probably does not exceed 2000°. The following figures are given by Féry for the temperatures in the flame of a Bunsen burner:—

Full draught.	Half draught.	Luminous.
1871° C.	1812° C.	1710° C.

With benzene vapour a temperature of 2000° C. is approached. Even if such high temperatures, nearly 3000°, were reached, a glance at Jellinek's figures for the rate of dissociation, of NO (p. 165) shows that very little of the extra yield could escape decomposition when the gases from the explosion bomb cool down, at the speed with which this could be effected. The alleged high yields are more probably to be sought in the faulty analytical methods used.

Bender, in applying the combustion method, proposes to burn fuel with air under a pressure of 4 atm. in a gas producer, the upper part of which is lined with a porous material which soaks up water. By the cooling produced by a water spray, and evaporation from the porous material, the 1 per cent. of NO produced is prevented from undergoing decomposition. The method sounds impracticable. He also proposes to burn methane in air enriched with oxygen, and the same method has been patented by Herman, who also suggests surface combustion on a zirconia mass. The gases are stated to contain 3 to 4 per cent. of NO by volume (which is probably incorrect, as will be shown below), and 1 kilo. of nitric acid is produced by the combustion of 2·5 cu. metres of methane. This works out at 105 grams nitrogen fixed per K.W.H., which is very high. But if we assume that only sufficient air is added to bring about perfect combustion of the methane according to the equation—

$$CH_4+2O_2=CO_2+2H_2O$$

we find that 1 volume of methane requires 10 volumes of air, and the gases after combustion and cooling occupy 9 volumes. For the combustion of 2·5 cu. metres of methane there would be required 25,000 litres of air, and the gas after combustion and cooling would occupy a total volume of 22,500 litres. The volume of NO corresponding to the stated yield of 1 kg. HNO_3 per 2·5 cu. metres methane is 208 litres, and the volume percentage of NO is, therefore, only 1–2 (as in the original Haüsser claims), and not 3–4, as stated. Herman's claims are therefore self-contradictory.

Experiments on the production of oxides of nitrogen in flames or gaseous explosions have been made by Haber and his students. In the explosion of a compressed mixture of hydrogen with equal volumes of oxygen and nitrogen, 3 molecules of nitric acid can be produced with every 100 molecules of water, *i.e.* 0·21 gram of nitrogen is fixed per 1 gram hydrogen burnt. By burning carbon monoxide in pre-heated air compressed to 8–9 atm., 3–4 molecules of NO are produced for every 100 molecules of CO burnt. With a mixture of equal volumes of nitrogen and oxygen instead of air, the yield is doubled. The production of oxides of nitrogen and nitric acid by the combustion of carbon monoxide in compressed air forms the basis of a patent of the Badische Co.

In connection with the high yields of oxides of nitrogen alleged to be formed in combustion and explosion reactions, it may be observed that, although most of the percentages claimed by inventors are doubtless imaginary, yet there is some evidence that even in the arc a yield in excess of the so-called equilibrium yield, as determined by Nernst and Jellinek, is sometimes obtained. Investigations of Haber and his students, in which the arc was produced at low pressure (100 mm.) in silica tubes cooled externally by water, showed that concentrations of over 10 per cent. of NO could be produced, although the temperature could not have exceeded the melting-point of iridium, viz. 2300° C., at which the "equilibrium" concentration of NO should only be about 2 per cent. The yield with the "chilled arcs" amounted to 57 grams HNO_3 per K.W.H. with a concentration of 3·5 per cent. NO; more recently 80 and 90 grams have been found. Some recent experiments by Island in which the gases expand adiabatically immediately after passing through the arc, and are thus very rapidly cooled, give yields of this order. Haber considers that the action of the arc is not purely thermal, but that an "electrical equilibrium" is also set up, owing to the kinetic energy of the electrons being imparted to the molecules by collisions. A more plausible explanation would appear to be that the so-called "equilibrium" values of Nernst and Jellinek were only apparent, on account of decomposition of the NO during cooling in their experiments. The higher values have all been found when special precautions to produce rapid cooling were taken.

At the same time it was known that oxidation of nitrogen to N_2O_5 occurs when air is exposed to the silent electric discharge (Warburg). Simultaneously the production of ozone is noticed, and it is possible that this is the active agent in bringing about the oxidation.

Ehrlich and Russ. (Brit. Pat. 10992 of 1912; *Wiener Monatshefte*, 1915, p. 317), by the silent discharge in closed vessels, obtained the following results :—

Gas used.	Per cent. NO in product.
Air 1 vol. O_2+4 vols. N_2 ..	.. 4·1
1 vol. O_2+1 vol. N_2 ..	.. 13·2
3 vols. O_2+1 vol. N_2 ..	.. 18

The velocity of formation of NO is practically the same with the different mixtures, but the rate of formation of ozone increases with the percentage of oxygen in the mixture. The NO is oxidised by ozone to N_2O_5, which in turn begins to break up when all the ozone is used up. (Cf. H. Spiel, "Ueber die Bilding von Stickoxyden bei der stillen elektrichen Entladung," Leipzig, 1911.) Other theories attribute the oxidation to the formation of "active nitrogen," which combines with the oxygen, but the experimental results of Strutt seem to disprove these.

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SECTION VIII.—AMMONIA AND AMMONIUM SALTS

Sources of Ammonia.—The chief sources of ammonia at present utilized are the following :—

(1) *By-product ammonia,* obtained by the destructive distillation, either without admission of air (gas-making, coke ovens, etc.) or with limited amounts of air and steam (producer-gas making), of nitrogenous organic matter such as coal, peat, bones, etc.

(2) *Cyanamide ammonia,* obtained by the action of steam or superheated water on calcium cyanamide, $CaCN_2$, which is formed when nitrogen is passed over heated calcium carbide—

$$CaC_2+N_2=CaCN_2+C$$
$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

(3) *Ammonia from nitrides,* such as aluminium nitride, AlN, which is treated with steam to produce ammonia in the Serpek process.

(4) *Synthetic ammonia,* obtained by the direct combination of nitrogen and hydrogen in the Haber process.

The first source is the one which has been longest in use, and until recently it was the only source of the ammonia of commerce. The name "ammonia" is said to have originated in the method of preparing *sal-ammoniac* by the distillation of camels' dung in the vicinity of the temple of Jupiter Ammon in the Libyan Desert, about the fourth century B.C., although this has been discredited by recent research. The old name for ammonium carbonate—"spirit of hartshorn"—has a similar origin, the substance being obtained by the destructive distillation of horns, bones, etc.

By-product Ammonia.—The most important sources of by-product ammonia are the following:—

(1) *From vinasse by the Vincent process* (see p. 278).

(2) *By the destructive distillation of bones in the manufacture of animal charcoal.*

The washed and dried bones are broken up, the grease is extracted by carbon disulphide, or a chlorinated hydrocarbon solvent such as pentachlorethane, or perchlorethylene, and the solid residue is distilled in iron or clay retorts. The gases are cooled and scrubbed with water, the gas passing on being burnt under the retorts. The condensed liquor separates into two layers—

(i) *An oil,* called Dippel's oil, amounting to about 1·7–2 per cent. of the weight of the bones, which has a very offensive odour and is used to some extent in Germany for denaturing alcohol;

(ii) *Ammoniacal liquor,* which is worked up as described under gas-liquor, with the production of 6–7 per cent. of ammonium sulphate, on the weight of the bones.

Horn, leather-clippings, wool, hair, and similar nitrogenous organic refuse may be treated in the same way as bones, or worked up for cyanides. Donath has proposed to heat such materials with the sulphuric acid residues from petroleum refining, as in the Kjeldahl reaction, with production of ammonium sulphate.

(iii) *By the destructive distillation of coal, peat, shale, and similar fuels containing nitrogen, in the preparation of coke and gas.*

Average coal contains about 1 per cent. of nitrogen, a portion of which is recovered in the form of ammoniacal liquor when the coal is distilled in the manufacture of illuminating gas or of coke. The average yield in the form of ammonium sulphate, in which form it is usually expressed, is 20–25 lbs. per ton of coal in both gas works and coke ovens; this represents less than 20 per cent. of the nitrogen in the coal recovered as ammonium salts. Up to

20 per cent. of the total nitrogen may be regarded as the maximum recovery in dry distillation, the rest of the nitrogen either escaping as elementary nitrogen or, in larger part, remaining behind in the coke.

The distribution of the nitrogen in coal among the products of dry distillation, in percentages of the total nitrogen is shown below :—

	Gas works.	Coke ovens.
Nitrogen in coke	58·3	43·31
,, in tar	3·9	2·98
,, as ammonia	17·1	15·16
,, as cyanides	1·2	1·43
,, as free N_2 in gas ..	19·5	37·12

The world's annual production of coal is about 1,000,000,000 tons, and the production of coke is about 100,000,000 tons, of which until recently only a small fraction was produced with recovery of ammonia. The loss of combined nitrogen in coal, expressed as ammonium sulphate, is therefore about 40,000,000 tons per annum, which is about 40 times the annual production of this salt. The use of recovery processes for the manufacture of coke was at first confined to the German practice, since there was a belief current among British manufacturers that coke produced in recovery ovens was unsuitable for smelting processes. After thirty years' success on the Continent, the suitability of coke from recovery ovens gradually dawned upon British users, with the result that rapid strides have been made of late years in the erection and working of recovery coke ovens. Of the 20,000,000 tons of coal annually coked in Great Britain, no less than 16,000,000 tons are now treated in recovery ovens.

Percentage of Coke Ovens working with Recovery of By-products.

	1900.	1910.	1916.
Great Britain	10	18	80
Germany	30	82	—
America	5	17	—

The production of ammonium sulphate, in tons, from by-product sources has been as follows :—

	1908.	1909.	1910.	1913.	1914.	1916.
Great Britain	321,500	348,500	369,000	432,000	421,000	—
Germany ..	313,000	340,000	375,000	550,000	—	—
America ..	40,000	90,000	116,000	177,000	—	1,000,000
France ..	52,000	53,000	56,000	75,000	—	—
Total ..	852,000	978,000	1,111,000	—	—	—

Of this ammonium sulphate, about 90 per cent. is utilized directly as a fertilizer for agricultural purposes, and the extension of agricultural practice contemplated in Great Britain will call for increasing production of the salt, although land which has been long under grass will doubtless, when opened up, require ammonia fertilizers to a less extent than land which has been long under cultivation.

The separate sources of supply of by-product ammonium sulphate in Great Britain in 1914 were as follows :—

Coke ovens	176,000 tons
Gas works	173,000 tons
Shale distillation	58,000 tons
Blast furnaces	16,000 tons
Other sources	8,000 tons
Total	421,000 tons

The dry distillation of coal with the production of coal gas in gas works, or of coke in ovens, cannot be described here, but a short account of the main types of coke ovens used is necessary in order to make clear the differences in procedure in working non-recovery and recovery ovens.

(1) *The Beehive Oven* is the primitive type and consists merely of a covered-in mound of brickwork, to which air is admitted and part of the fuel in the oven is burnt to produce the heat necessary to carbonize the rest. Attempts to work such ovens with recovery have been made, but without success, since the tar obtained from beehive ovens, in which air is admitted, is quite different from the tar produced from coal in gas making.

(2) *The Coppée Oven* (1872) works on the recovery system. Each unit consists of a 30-ft. long narrow closed chamber with thin ($2\frac{1}{2}$–3 in.) walls externally heated with gas. Coal is pushed in, and coke out, by means of rams. The gases and vapours are led off from the centre by a main and scrubbed. The scrubbed gases mix with air and heat the coking chambers from outside by passing through vertical flues between them. These ovens did not give a satisfactory metallurgical coke, and were subsequently modified. There are two main modifications—

(i) *The Otto-Hoffmann Oven* (1881), which uses Siemens' regenerative principle with a modified Coppée oven.

(ii) *The Otto-Hilgenstock Oven* combines preheating of the air with a low pressure of the gases, which are burnt below the oven in large Bunsen burners. In a modern oven $7\frac{1}{2}$ tons of coal are coked in 36 hours, with an average yield of 72·2 per cent. of coke. The cost per unit, complete with recovery plant, is about £300.

(3) *The Carvès Oven* (1862) was much improved by Simon, of Manchester, and the Simon-Carvès type, with recuperators, was introduced in 1883. This oven is heated by horizontal flues between the ovens. A modification largely used in Belgium, France, and America is the *Semet-Solvay oven.* The *Hüssner oven* is a modification used in Germany. The coke yield in British practice with Simon-Carvès ovens is—

Durham coal	77 per cent.
Accrington coal	69 per cent.
Staffordshire coal	52 per cent.

The yield of ammonia is 1·0–1·25 per cent., expressed as sulphate on the weight of the coal, with North country coal, and 2 per cent. with Staffordshire coal. In German practice the corresponding figures are 65–75 per cent. and 0·924–1·1 per cent. Another modification of this oven is the *Koppers oven,* and the following particulars relate to a small English coke-oven set of the Koppers type (1908) :—

Number of ovens: 40.

Output: 1963 tons wet, or 1850 tons dry, coal coked per week.

Cost of plant, including coal crushing and benzol plants: £53,000.

Gas per ton of coal: 11,700 cu. ft. of 560 B.T.U. debenzolized to 2¾ gallons crude benzol per ton.

Surplus gas: 50 per cent. of gas made, *i.e.* 1,638,000 cu. ft. per day maximum.

Ammonia yield: 34·5 lbs. sulphate per ton dry coal (30 per cent. recovery).

The following particulars relate to beehive and Semet-Solvay ovens in use at Syracuse, N.Y. (1895):—

	Beehive.	Semet-Solvay.
Number of ovens	12	12
Average time of coking	51·5 hours	20 hours
Coke produced in 24 hours	27·76 tons	71·69 tons
Tar produced in 24 hours	nil	2·65 tons
Ammonium sulphate per 24 hours	nil	0·772 ton
Yield of coke per cent.	62·3	80·7
Yield of tar per cent.	0·0	3·69
Yield of $(NH_4)_2SO_4$ per cent.	0·0	1·075
Cost per oven	£63	£320
Life of oven	5 years	10 years
Cost of oven per ton coke	5·52*d.*	4·2*d.*
Value of products per ton coal	10s.	£3 1s. 8*d.*

The conditions leading to the formation of ammonia in the manufacture of illuminating gas by the distillation of coal have been summarized as follows by Simmersbach:—

(1) The formation of ammonia occurs chiefly at a temperature when the caking of the coal has been completed.

(2) The formation of ammonia has its maximum at different temperatures for different coals.

(3) This maximum temperature varies with the nature of the nitrogen compounds in the coal, and is between 800°–900° C.

(4) Decomposition of ammonia in a concentrated gaseous state begins appreciably at 750° and is about complete at 800°. But in the destructive distillation of coal, the ammonia comes off in a dilute state, decomposition does not begin till 900°, and is increased by rise of temperature.

(5) The formation of cyanogen increases with the quantity of ammonia and the temperature.

(6) The quantity of cyanogen formed is about 1·2 per cent. of the total nitrogen in the coal, and about 5 per cent. of the ammonia formed.

(7) The presence of water vapour lowers the cyanogen and increases the ammonia.

(8) High speed of gas flow retards the formation of cyanogen and decomposition of ammonia.

(9) The dimensions of the pieces of coal have no influence on the formation of ammonia.

The distillation of *shale* has been carried out in Scotland for the production of oil and tar for a considerable number of years. In 1865 Bell commenced to recover the ammonia as sulphate. According to Young and Beilby, Scotch shale yields on distillation—

(1) *Dry distillation in retorts* :—	(2) *Steam afterwards blown through the red-hot retorts* (1·28 steam to 1 part shale) :—
20·4 per cent. total N in the tar.	20·4 per cent. total N in the tar.
62·6 ditto in the coke.	4·9 per cent. ditto in coke.
17·0 per cent. as ammonia.	74·3 per cent. as ammonia.

The greatly increased yield of ammonia when steam is blown through the incandescent coke is evident, and the same result will be found also in considering the gasification of coal by the Mond process in a later section.

If the "acid-tar" produced is neutralized with lime and distilled, a "neutral tar" is produced, and 21 per cent. of the nitrogen content of the tar given off as ammonia.

The addition of lime to coal and shale before dry distillation is stated to increase the yield of ammonia, but in spite of numerous communications on the subject this simple problem seems still to be under discussion.

The Gasification of Fuel by the Mond Process.—A great economy in the combined nitrogen of coal was effected by executing the gasification in gas producers in the presence of air and steam at comparatively low temperatures (L. Mond, 1883). In the Mond process a mixture of air and steam is drawn at a low red heat over fuel, contained in a large upright iron cylinder, having a water-seal at the bottom from which the ashes are removed, and a hopper for fuel and an outlet pipe for gas at the top. A mixture of hydrogen, carbon monoxide, carbon dioxide and nitrogen (from the air) is produced—

$$C+2H_2O \rightleftarrows CO_2+2H_2 \text{ (below } 900^\circ \text{ C.)}$$
$$C+H_2O \rightleftarrows CO+H_2 \text{ (high temperatures)}$$

About 3–4 times as much nitrogen is recovered in the form of ammonia in the Mond process as in the dry distillation of coal.

Process.	Weight of ammonia from 100 kilograms coal.	Per cent. recovery of ammonia.
Dry distillation	.. 0·25–0·3 kg.	20
Mond gasification	.. 0·75 kg.	60

About 1,000,000 tons of coal are annually gasified by the Mond process in Great Britain; on the Continent less is so treated. At Northwich, shortly after the installation of Mond producers, ammonium sulphate was obtained for £4 10*s*. 0*d*. to £5 0*s*. 0*d*. per ton, which was less than half the market price, and the regularity introduced by gas firing was found advantageous. About 1890 superheating of the air and steam entering the producers was introduced, and the calorific power of the gas, which was previously rather low, was increased, together with the yield of ammonia. The calorific power of Mond gas is always rather low, but against this must be set its cheapness, and the clean character of the gas in burning, as well as the recovery of the by-products. Very large gas engines are required for economical working. In the old type of washer used by Mond, consisting of towers packed with ring tiles over which dilute sulphuric acid was dropped, the acid strength had to be kept low, as otherwise the solution of ammonium sulphate was discoloured.

The most recent type of gas producer on the Mond principle is that of Lymn, in which various improvements of the original type have been made :—

(1) The tall scrubbing towers are replaced by vertical

intensive mechanical washers, utilizing the momentum of the gas.

(2) Dust is removed by a cyclone dust separator.

(3) The producers are redesigned, and fitted with rotary grates and mechanical ash removers.

(4) In the Mond system 2½ tons of steam have to be used per ton of coal gasified, of which two-fifths is recovered in cooling the gas, but 1½ tons must be made in boilers. It is therefore advantageous to use waste steam. Lymn obtains this by utilizing the waste heat in the exhaust gases from the gas engines, and so generates steam in 25 per cent. excess over the requirements of the producer.

A description of a modern Lymn plant is given by the inventor as below :—

Capacity : 2812–2830 K.W. as gas.
Consumption of coal (0·8 per cent. N) : 64·6–70·2 tons per 24 hours.
Cost of coal : 12*s.* 4*d.* to 13*s.* 5*d.* per ton.
Cost of gas per K.W.H., including 10 per cent. amortization : 0·07*d.*

It has been stated that the yield of ammonia is increased by chilling the outside of the producer with water.

In 1907 Dr. Nicodemus Caro, of Berlin, took out a patent for the application of the Mond process to the gasification of low-grade coal, coal washings, and pit-head waste ("Heap-Coal") containing as low as 30 per cent. of coal. Such waste coal gives 25–30 kg. ammonium sulphate per ton, and 50–100 H.P. hours as electric current. It is doubtful if any attempt has been made in this country to utilize the enormous heaps of waste coal lying near the pit-heads, yet it should be possible to gasify this waste fuel with full recovery of the ammonia, and the power could be utilized in the preparation of cyanamide or other product dependent on cheap power. There seems more hope for such a scheme, involving the preparation of cyanamide, its decomposition with production of ammonia, and the oxidation of this ammonia to nitric acid, than there is for the arc process. The tendency in the past has been to limit all power considerations to the use of high quality coal, which may be far too expensive. The use of lignite (which is not found to any extent in this country, but is plentiful in the colonies) has been applied to direct steam raising at Bitterfeld, Saxony, where 3000 H.P. was produced for the electrolytic alkali process in 1894. Lignite has also been used for gas producers in North Dakota, America. The utilization of low-grade fuel is a problem which calls for more attention than has been given to it in England. On account of the plentiful supply of good coal found here, it has been unnecessary to trouble about the poorer fuel; but this position cannot be maintained any longer if processes dependent on very cheap fuel are to be introduced with success.

The application of *peat*, or *turf*, in gas producers was also pointed out by Frank and Caro in 1908. The wet peat containing up to 60 per cent. moisture is gasified at 300° in lagged vertical iron Mond producers. The temperature rises to 500°, but the optimum temperature is 400° when ammonia recovery is aimed at. Dried peat contains about 1–2 per cent. of nitrogen. The gas obtained at Osnabruck by the Frank-Caro process has a calorific value of 1400 Cal. per cu. metre, and 70 per cent. of the nitrogen is recovered as ammonia. The value of this ammonium sulphate was said to cover the whole cost of production, and the power was obtained free. Whether this is true or not, the attitude formerly adopted in this country towards the gasification of peat, namely that peat containing more than 30 per cent. of moisture could not be gasified directly, and that the drying off of the rest of the water from the wet peat containing 70 or more per cent. of water was an operation which made large-scale working impossible, has been shown to be quite incorrect. Producers are now working in Ireland with peat containing 60 per cent. of water. At Portadown peat costing 5*s*. per ton is gasified with the production of power at $\frac{1}{16}$*d*. per H.P. hour. In Italy, at Orentano near Pisa, a plant for the gasification of peat, with a capacity of 300 K.W., has been in operation since 1910, and was laid down by a British company.

	England and Ireland.	Italy.	Germany.
Moisture in wet peat	58–63	15	40–60
Percentage N in dry peat	2·2–2·3	1·58–2·5	1·0
Ammonium sulphate per ton dry peat in lbs.	168–215	115–175	70

The difficulty of the process does not lie in the gasification, but in the supply of the peat and the drying off of the water. Peat cutting by hand is a slow and somewhat expensive process and mechanical peat cutters are still in the experimental stage. The peat as dug contains 30–90 per cent. of moisture, and is usually dried down to 20 per cent. This is, however, difficult in a moist climate. Experiments have been made with the object of drying peat by forcing out the liquid water by means of an electric current, applied to produce electric osmose.

The Lymn producers with preheated air and steam are stated to use peat containing 40–60 per cent. of moisture directly.

About 10,000,000 tons of peat are raised annually, 4 of which are produced in Russia, the whole representing 90,000 tons of ammonia. Extensive areas of peat occur in Canada, and in Ireland where it forms 5·8 per cent. of the soil. In Finland peat forms 20 per cent. of the soil. In Prussia there are 6,000,000 acres of peat land, and in America 140,000 sq. miles, representing probably 13,000 million tons of peat or 640 million tons of ammonium sulphate. In England there are 6 million acres of peat bog of an average depth of 12 ft., in Ireland there are 3 million acres, some being very deep. Scotch peat usually yields 30·2 lbs. ammonium sulphate per ton; Doncaster peat 21 lbs., on the wet peat.

Other methods of treating peat (Grouven, Woltereck) have not been successful.

Similar to peat is the *silt* which accumulates by subsidence at the mouths of rivers. At the mouths of German rivers the silt contains as much as 2 per cent. of combined nitrogen, which could be recovered by gasification. This combined nitrogen is the cause of the fertility of the soil deposited by rivers in India and Egypt, and utilized in agricultural practice from the remotest antiquity.

Ammonia from Blast Furnaces.—Ammonia is present in the gases from blast furnaces using coal in iron smelting; a portion is probably formed by hydrolysis of the cyanides produced in the furnace. The difficulty of recovery depends on the necessity of cooling and washing the very large volumes of gas passing through the furnace, but in Scotland and Staffordshire this is effected by spraying water through the gas as it passes through large brickwork chambers. Works using coke for smelting do not recover ammonia. In most cases an ordinary ammonia still is interposed between the furnaces and the regenerative stoves where the gas is burnt.

Production of Ammonia from Gas Liquor.—The ammonia-water or ammoniacal liquor from gas or coke oven works is a very complex product, containing besides tar, phenol, naphthalene, pyridine, etc., the following salts of ammonia :—

I. *Volatile Salts*—expelled by boiling alone :—
ammonium carbonates (mono-, bi-, and sesqui-).
,, sulphide and hydrosulphide.
,, cyanide.
,, acetate (?).
,, hydroxide.

II. *Fixed Salts*—decomposed by lime :—
ammonium sulphate.
,, sulphite.
,, thiosulphate.
,, thiocarbonate.
,, chloride.
,, thiocyanate.
,, ferrocyanide.

Its composition is very variable; some analyses gave the following results:—

Total ammonia	17·154	grams per litre.
Volatile „ ..	14·046	„ „
Fixed „ ..	3·088	„ „

The amounts of ammonia are usually given in what is known as "ounce strength," this curious unit being the number of ounces avoirdupois of pure sulphuric acid required to neutralize the ammonia in 1 gallon of liquor. Volumes of liquor are then converted to equivalent volumes of 10-oz. liquor.

The ammoniacal gas liquor, after separation of the tar by settling in tanks, is worked up into the following products:—

(1) Concentrated gas liquor.
(2) Purified ammonia solution ("aqua ammonia," or "ammonia spirit").
(3) Ammonium sulphate.
(4) Anhydrous liquid ammonia.

In the early days of gas-works ammonia recovery, the gas liquor was neutralized directly with sulphuric or hydrochloric acid, when very impure and tarry salts were produced. In the newer practice, the ammonia is always distilled out first and then neutralized with acid. The free ammonia is driven out by boiling alone, and the fixed ammonia then obtained by adding an excess of lime and continuing the boiling. About 350 parts of lime to 100 parts of fixed ammonia are used. In small works caustic soda is used instead of lime, as it is less troublesome, or else the fixed ammonia, which is an appreciable fraction of the total, is not recovered at all. Formerly this was the case in large works, because in the old direct-fired stills crusts were formed when lime was used to liberate the fixed ammonia, and prolonged boiling was necessary to drive off all the ammonia. In such an old still apparatus, of the total ammonia—

76·9 per cent. was expelled by boiling alone;
20·5 per cent. was recovered by boiling with lime;
2·6 per cent. was left in the still-liquor.

With modern apparatus, such as is described below, less than 0·005 per cent. of ammonia is contained in the waste liquor.

Ammonia was also produced by blowing steam into coke towers fed with gas-liquor.

In modern practice the distillation is carried out in column apparatus on the principle of the Coffey still, the firing being either direct external (coal, etc.), or by steam coils, or by live steam blown into the still. The last method is to be preferred, because external firing causes crusts of lime salts to form in the still, whilst steam coils are less economical than live steam. Only 1–2 per cent. of the total ammonia recovered is estimated to be made in direct-fired stills at the present time.

A still of modern type is that of Grüneberg and Blum, shown in Fig. 53, which combines many improvements introduced from time to time in the old stills. Most of the ammonia is now recovered as sulphate, and the working of the Grüneberg and Blum still for the preparation as sulphate will first be described.

The plant consists of four parts: the still A, the heat economizer B, the lime pump C, and the saturator D.

The liquor enters the economiser through the pipe 1, and is heated by the gases coming from the saturator (where the ammonia is dissolved in sulphuric acid), and passes by 2 to the still column 3 containing diaphragms. Steam is passed up this column and bubbles through the central pipes 4 covered with serrated hoods. The volatile ammonia is expelled in the upper part of this column, and lower down at 5 milk of lime of density 15°–22° Tw. is added from the pump, which expels part of the fixed ammonia. The liquor then runs to the boiler 6, containing a stepped cone over which the liquor flows in thin layers and is heated by the steam coils 7. The liquor in the economizer is heated by the hot gases from the saturator passing through the bell 8 and the pipe 9, the liquor entering the inner pipes at 10, rising through B and passing through 2 to the column. The liquor then passes down the column to the lime vessel 5, overflowing by a pipe 12 to the sludge catcher 13, whence it overflows all round 13 and runs over the stepped cone 14, discharging from 15 to the overflow 16. Steam travels in the opposite direction to the liquor, passing up the steps of 14, up the pipe 17 into 18 and the lime vessel 5, from which the mixed steam and ammonia pass up the column and, after separation of much of the steam by liquefaction in the cool upper part of the column, the gas leaves by the pipe 19 to the saturator. The uncondensed gases (H_2S,

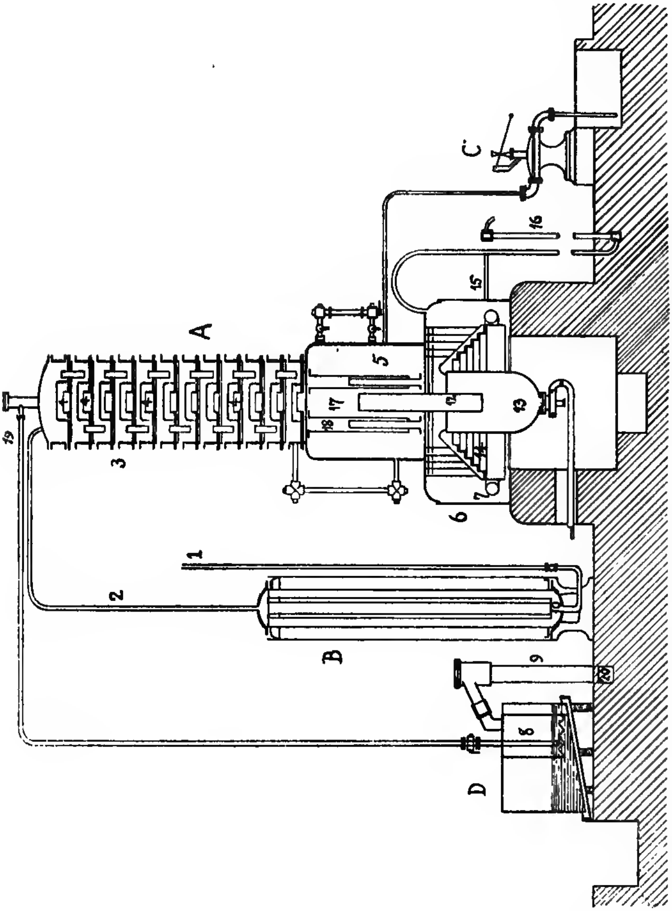


FIG. 53.—Grüneberg and Blum Ammonia Still.
A, still; B, preheater; C, lime pump; D, saturator.

etc.) collecting in 8 pass to the flue 20 and the economizer, and finally to the burners to produce SO_2, or else to oxide of iron purifiers, from which sulphur is recovered in the Claus process.

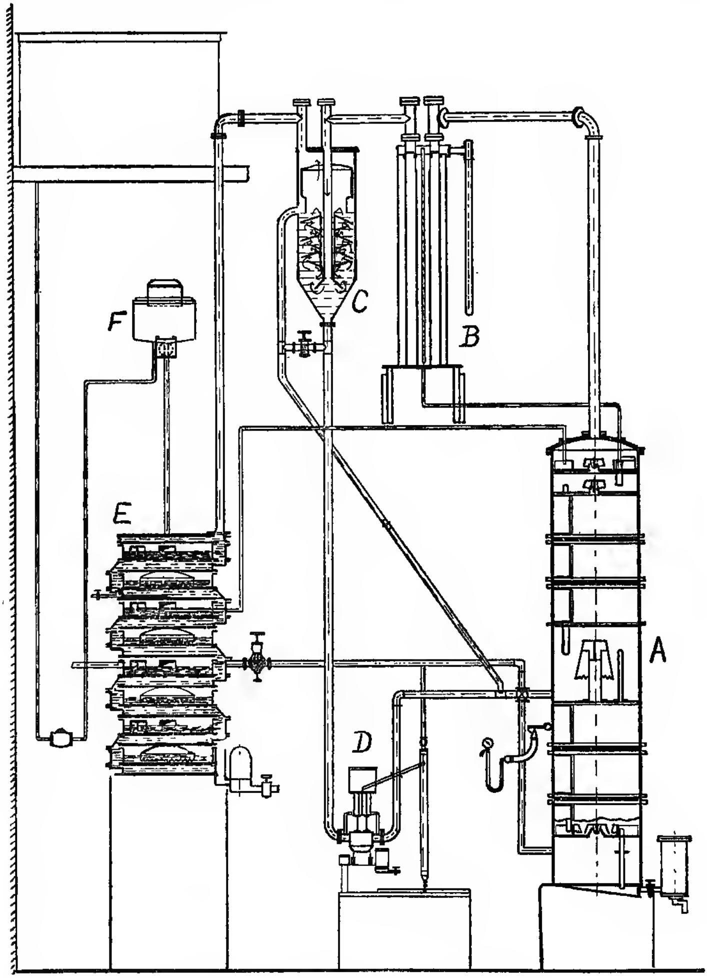


FIG. 54.—" Bamag " Ammonia Still.

A, still; B, economizer; C, lime washer; D, lime pump; E, cell-condenser; F, liquor feed.

The Feldman apparatus is similar to the above, but two columns are used: in the first the volatile ammonia is driven off, then milk of lime is added and the sludge settles; in the second column, to which the settled liquor passes, the ammonia is driven out by steam. This type is said to be very successful. A Feldman apparatus in use at Runcorn deals with 200 tons of liquor daily.

In the apparatus of the "Bamag" (Fig. 54) one column is used, and milk of lime introduced into a lower compartment where the bubbler is deeper in the liquid, so that the latter is more efficiently stirred.

The Solvay apparatus consists of a column with sections carrying inverted saucers. Preheated liquor runs in at the top and steam is passed in at the bottom, which drives out the ammonia. Lower down, milk of lime is added and the remaining ammonia is driven out. The vapours may pass through a reflux cooler, or the top of the column may be cooled by water, if a concentrated liquor is required.

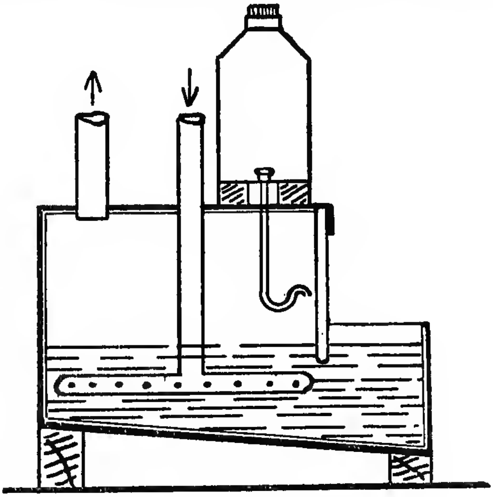


FIG. 55.—Ammonia Saturator.

The absorption is carried out in a lead vessel, or in one of iron or wood lined with lead, containing sulphuric acid of 60° Bé. and having a sloping floor as shown in Fig. 55.

The gases are led in through a perforated pipe into the closed half, which is separated from the open half by a seal partition dipping into the acid. The ammonium sulphate crystals are raked on to draining shelves and the liquor runs back to the saturator. Fresh acid is added from a vessel above the saturator. The crystals are 93–99 per cent. purity, containing 0·1–0·5 per cent. of free acid. The colour should be white or grey. The sulphuric acid used should be brimstone acid or dearsenicated acid, as otherwise arsenic sulphide is produced which colours the salt yellow. A blue colour is sometimes produced if the gas is passed into the acid too rapidly, when local alkalinity, leading to the formation of cyanides and thence Prussian blue, is the result.

Ammonium sulphate is now largely produced by the so-called Direct Process, in which the tar is separated from the crude gas by special apparatus, and then the gas passed directly into sulphuric acid to produce ammonium sulphate.

In the processes of Feld and Burkheiser an attempt was made to utilize the sulphur in the crude gas to produce ammonium sulphate with the ammonia. In the Feld process the gas is washed with hot tar, and then passed into a solution of ferrous or zinc sulphate—

$$FeSO_4+2NH_3+H_2S=FeS+(NH_4)_2SO_4$$

The FeS (or ZnS) is filtered off and treated with a dilute solution of sulphurous acid, when thiosulphate or tetrathionate is formed—

$$2FeS+3SO_2=2FeS_2O_3+S$$
$$FeS+3SO_2=FeS_4O_6$$

These salts act on ammonia and sulphuretted hydrogen in the same way as the sulphate, and FeS is precipitated. The solution contains ammonium *sulphite*. When sufficiently concentrated the solution is treated with SO_2 and "ultimately" yields ammonium *sulphate*. In the later process of Feld the tar fog is separated by treatment with atomized liquid tar at 100°–200°, and then with steam. On cooling to 40° hardly any ammonia is condensed, and this can be absorbed in the usual way. In the process of Burkheiser the tar-free gas is led over oxide of iron catalyst, when the H_2S is oxidized to SO_2, which then reacts with the NH_3 to give ammonium sulphite. Cobb precipitates a solution of $ZnSO_4$ with the gas, when zinc sulphide and a solution of ammonium sulphate are formed. The ZnS on roasting gives ZnO and SO_2. The ZnO when suspended in water and treated with SO_2 gives zinc *sulphite*, and this with gas containing NH_3 and H_2S gives ZnS and ammonium *sulphite*.

All these direct processes are at present on trial, and further details cannot be given. It will be noticed that the product is usually ammonium sulphite, not sulphate, and this must be oxidized. According to a Badische patent, this can be effected in presence of selenium as a catalyst—

$$3(NH_4)_2SO_3+6NH_4HSO_3=6(NH_4)_2SO_4+3S+3H_2O$$

The direct process in which tar-free gas is led into dilute sulphuric acid appears to be successful.

In the production of ammonia from gas liquor, the latter is distilled. Three products are made :—

(1) *Concentrated Gas Liquor.*—This is made for use in the Ammonia-Soda Process in two qualities.

(*a*) Containing 16–18 per cent. NH_3 together with sulphide and carbonate. The gases from the ammonia still are passed through a reflux condenser and then through a direct condenser. One form of condenser is the cell-cooler (Fig. 52), in which gas liquor is preheated in serving as the cooling medium. As reflux condenser, a large metal Liebig's condenser is often used.

(*b*) Containing 18–26 per cent. ammonia with a little sulphide but no carbonate. The vapours from the still pass through a lime-washer, in which milk of lime is pumped over plates in a small tower, through which the spent lime runs to the still (Fig. 52). The traces of sulphide form a protective coating of iron sulphide on the iron pipes used in conveying the liquors in the ammonia-soda process.

(2) *Purified Ammonia Solution* or *Ammonia Spirit.*—Excess of lime (from 3 to 3½ times as much as is used in making ammonium sulphate) is added to the still to allow for hydrolysis of calcium sulphide—

$$CaS+2H_2O \gtreqless Ca(OH)_2+H_2S$$

Even then a trace of H_2S comes over from the still and must be removed by adding ferrous sulphate to the lime-washer, when FeS is precipitated, and not being very soluble is not hydrolysed like calcium sulphide. The gas from the still may also be passed through a 10 per-cent. solution of caustic soda after the lime-washer. The gas is then passed through layers of wood charcoal, and finally through a washer containing a heavy mineral oil to remove pyridine and other organic bases. The pure gas is led into distilled water until a 30-per-cent. solution is produced. The solution must be cooled during absorption, as much heat is set free. The wood charcoal needs frequent renewal, but may be revived by heating to redness in closed iron retorts.

In the process of Hill, the crude liquor is heated to 70°–80° before passing to the still, when much of the CO_2 and H_2S is set free and escapes, thus effecting economy of lime and minimizing the choking of the still column with lime salts—

$$(NH_4)_2S+2H_2O=2NH_4OH+H_2S$$
$$(NH_4)_2CO_3+H_2O=2NH_4OH+CO_2$$

(3) *Anhydrous Liquid Ammonia.*—The purified and dried ammonia gas is compressed into steel coils. All parts of the apparatus must be of steel to prevent corrosion, and with multistage compression the heat is removed at each stage. The gas is then passed to cooling coils immersed in cold water for liquefaction. The liquid, of 99·9 per cent. purity, is sent out in steel bottles of 20, 50, or 100 lbs. It is used for refrigeration, and in the preparation of sodamide, $NaNH_2$, by passing ammonia gas over heated sodium. Sodamide is used in the manufacture of artificial indigo and of cyanides.

By cooling 49 per cent. and 65·4 per cent. ammonia solutions in liquid air, Rupert obtained the crystalline compounds NH_4OH and $(NH_4)_2O$, melting at $-77°$ and $-75°$ respectively.

Ammonium Salts.—Ammonium salts of technical importance are—

The sulphate, $(NH_4)_2SO_4$, already described;
The chloride, NH_4Cl, or "sal ammoniac;"
The carbonates;
The nitrate, NH_4NO_3;
The phosphates, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$.

Ammonium chloride is produced:—

(1) By neutralizing "Concentrated gas liquor" with hydrochloric acid, evaporating and crystallizing.

(2) By double decomposition of the sulphate with common salt and "fishing" out the sodium sulphate as the liquid is boiled down—

$$2NaCl+(NH_4)_2SO_4=Na_2SO_4+2NH_4Cl$$

(3) In solution for use as a flux by passing a mixture of CO_2 and NH_3 into a solution of calcium chloride:—

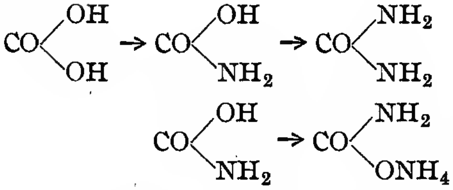
$$CaCl_2+2NH_3+CO_2+H_2O=2NH_4Cl+CaCO_3$$

Ammonium chloride is sometimes sublimed in iron pots with concave iron lids; it forms tough fibrous masses often coloured yellow in places by ferric chloride. The salt is also pressed into blocks or tablets—"voltoids"—for use in batteries.

Ammonium Carbonate.—The following salts have been isolated and examined by Divers:—

(1) Neutral carbonate, $(NH_4)_2CO_3$;
(2) Semiacid carbonate, $(NH_4)_4H_2(CO_3)_3+H_2O$;
(3) Acid carbonate, or bicarbonate, NH_4HCO_3.

Commercial "carbonate of ammonia" is a mixture of the bicarbonate and ammonium carbamate, a derivative of the monamide of carbonic acid (the diamide is urea)—



$$\mathrm{CO}\!\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. \rightarrow \mathrm{CO}\!\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right. \rightarrow \mathrm{CO}\!\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right.$$

$$\mathrm{CO}\!\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right. \rightarrow \mathrm{CO}\!\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{ONH_4}\end{matrix}\right.$$

Ammonium carbamate.

The commercial salt usually contains 31 per cent. NH_3 and 56 per cent. CO_2. It is prepared by heating a mixture of 1 part ammonium sulphate with 1·5–2 parts of chalk in an iron retort, and passing the vapour into a lead chamber, where crusts of ammonium carbonate collect. The salt is used in wool-washing, in the preparation of baking-powder, and of "smelling-salts."

Ammonium Nitrate is made :—

(1) By neutralizing nitric acid with ammonia, or by blowing ammonia gas into 60 per cent. nitric acid, in covered pans, when the heat developed is sufficient to drive off all the water produced in the reaction—together with about 20 per cent. of the ammonium nitrate.

(2) By decomposing the sulphate with sodium nitrate in aqueous solution. Careful attention must be paid to the concentrations and temperature, the whole process being regulated by the use of phase-rule diagrams showing the phases separating at the various temperatures and compositions.

(3) By decomposing calcium nitrate with ammonium carbonate. The calcium nitrate is made by the double decomposition of sodium nitrate and calcium chloride, "fishing out" the sodium chloride which separates from the hot liquor. The Norwegian calcium nitrate is said to give less satisfactory results than that prepared as described, possibly because it is slightly basic and contains iron.

Ammonium nitrate is largely used in the manufacture of explosives.

Ammonium phosphate is prepared by treating superphosphate of lime with water and steam to produce a liquid of density 42° Tw. This is decomposed with barium carbonate to precipitate sulphates, and neutralized with a slight excess of ammonia. On evaporation the monophosphate, $NH_4H_2PO_4$, separates. On adding more ammonia, the diphosphate, $(NH_4)_2HPO_4$, used in sugar refining, is produced.

Ammonium thiocyanate, NH_4CNS, occurs in gas liquor and in spent oxide from the purifiers. It is prepared by washing the crude gas, containing ammonia and cyanides, with water containing powdered sulphur in suspension. The ammonium sulphide produced reacts with hydrocyanic acid to form the ammonium salt of thiocyanic acid, NH_4CNS, in 30–50 per cent. solution. This is purified by adding barium chloride, recrystallizing the barium thiocyanate, and decomposing in solution with ammonium sulphate. Ammonium thiocyanate, often called the sulphocyanide, is used in photography.

Ammonia from Cyanamide.—Berthelot in 1869 observed that acetylene, under the influence of the electric arc, combines with nitrogen to form hydrocyanic acid—

$$C_2H_2+N_2=2HCN$$

After the discovery that metallic carbides are formed by heating the oxides with carbon in the electric furnace, *e.g.* calcium carbide—

$$CaO+3C=CaC_2+CO$$

and that carbides with nitrogen gave cyanides, the old puzzle as to the formation of cyanides in the blast furnace was cleared up.

Frank and Caro in 1895 showed that in the formation of barium cyanide from barium oxide, carbon, and nitrogen at high temperatures, the following stages are passed through :—

$$(1)\quad BaO+C=Ba+CO$$
$$(2)\quad Ba+2C=BaC_2$$
$$(3)\quad BaC_2+N_2=BaCN_2+C$$

followed, under favourable conditions by the reaction—

$$(4)\quad BaCN_2+C=Ba(CN)_2$$

The intermediate substances, of which $BaCN_2$ is a type, were discovered by Rothe and Freudenberg, and are called *cyanamides*, since they are derived from the amide of hydrocyanic acid.

$$\underset{\text{cyanamide}}{H_2N{-}N{\equiv}C} \rightarrow \underset{\text{barium cyanamide}}{BaN{-}N{\equiv}C}$$

The corresponding calcium compound, calcium cyanamide, or as it is usually called simply, "cyanamide," is produced by passing nitrogen over calcium carbide at 1100°—

$$CaC_2+N_2=CaCN_2+C$$

When the technical production of calcium carbide was begun in 1895, the possibility of using these reactions in the fixation of atmospheric nitrogen became apparent, and in 1904 the cyanamide industry was founded. The first factory was completed in 1906, but the industry received an important impetus in 1910, when steady production began at Niagara, and cyanamide works are now in operation in various parts of the world.

In 1907 Erlwein showed that it was not necessary to start with calcium carbide, since a mixture of coke and lime when heated in the electric furnace absorbed nitrogen passed over it, with formation of cyanamide—

$$CaO+2C+N_2=CaCN_2+CO$$

When the demand for carbide fell off, after the disappointment attending the use of acetylene gas as an illuminant, it was found cheaper to use carbide in the original process of Frank and Caro rather than Erlwein's process, and the older process is now almost exclusively used.

In the cyanamide works at Odda, in Norway, the crushed carbide is heated in relatively small drums of sheet iron, lined with refractory bricks, by means of carbon rods passing down the axes of the drums and heated electrically. A number of drums are enclosed in an air-tight chamber, and nitrogen passed in. When absorption has begun, the current is turned off, and the heat of reaction maintains the material at a sufficiently high temperature, which has to be carefully regulated. After 30–40 hours the drums are withdrawn, allowed to cool, and the blocks of cyanamide removed. This is then ground to powder, treated with water to remove carbide, and packed in bags. Sometimes the powder is treated with oil to render it less dusty. It contains about 20 per cent. of nitrogen, and comes on the market as "Nitrolim." The nitrogen is prèpared by the fractionation of liquid air in a Linde machine.

Cyanamide works have been established in other parts of Norway, in America, and in Italy. It is estimated that carbide works which pay £2 to £2 10s. per H.P. year for power, and average prices for coke, lime and nitrogen, can produce cyanamide at a profit.

In the continuous cyanamide process of Tofani the crushed carbide is conveyed to the top of a vertical shaft furnace by a worm-feed, falls down over sloping plates after heating by passing through a row of arcs or resistance electrodes in the upper part of the furnace, and meets a stream of nitrogen passing up the furnace. The cyanamide is withdrawn from an air-tight chamber at the bottom. In the improved process, now in operation in Norway, the arcs are replaced by electrodes of carbon, 350 mm. diameter, the consumption of electrodes being 3·75–5·5 kg. per ton of cyanamide. The product is very uniform and contains 19–20 per cent. nitrogen. One ton of cyanamide is produced from 725 kg. of carbide.

When cyanamide is treated with superheated steam or water, ammonia is produced—

$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

In the American process, used at Syracuse, N.Y., the cyanamide is decomposed as follows. 12,000 lbs. water and 7000 lbs. cyanamide are placed in an autoclave and agitated for an hour to remove acetylene from unchanged carbide. Two per cent. of slaked lime and 3½ per cent. of soda are then added, and steam admitted to 3–4 atm. pressure for 15 minutes. The pressure rises automatically owing to production of ammonia, to 12–14 atm. in 20 minutes.

The ammonia is discharged gradually, so as to maintain the pressure, and after 1½ hours steam is again admitted to 6–8 atm. and the ammonia again removed. Further steaming may recover a further 2 per cent. of ammonia. The yield is 98 per cent. The ammonia is washed with a solution of caustic soda to remove silicon and phosphorus compounds from the calcium silicide and phosphide usually present in the carbide, and is then very pure. The gas may be stored as such in a gasholder over water covered with a layer of oil, or converted into an aqueous solution.

The world's production of cyanamide in 1914 was 300,000 tons. Works have been erected in Germany since the outbreak of the war for the production of 500,000 tons, as well as arc process works and the Haber synthetic process. Fair progress has also been made in America.

Various sources of information show that the power consumption in the cyanamide process is 20 K.W.H. per kg. of nitrogen fixed (see tables at end of this section). The cost at Odda is stated to be £4 10s. 6*d*. per ton; that at Bussi (Italy) £4 0s. 0*d*. per ton, in both cases for 20 per cent. nitrogen content, which work out at 2·75*d*. and 2·43*d*. per lb. fixed nitrogen, respectively.

The following table gives an approximate estimate of the amounts of nitrogen fixed by the different processes :—

	1913.	1916.
Cyanamide	65,000 tons	209,000 tons
Arc	18,590 ,	29,510 ,,
Haber	8,000 ,,	60,000 ,,

In 1916, one million horse-power was expended in the fixation of nitrogen.

Ammonia from Nitrides.—Many elements combine directly with nitrogen when heated in the gas, with formation of nitrides. Nitrides are so produced from lithium, magnesium, barium, calcium, boron, titanium, silicon, and aluminium.

Of these, the nitrides of titanium, aluminium and silicon have been utilized in the manufacture of ammonia, which is produced when the nitrides are treated with water or steam under suitable conditions.

In Landmark's process, steam and nitrogen are passed alternately over a mixture of titanium nitride and carbon—

$$2TiN_2+3C+3H_2O=2TiN+3CO+2NH_3$$
$$2TiN+N_2=2TiN_2$$

According to Schukow (1908), titanium nitrides are more probably solid solutions.

In a Badische process, 75 parts of silica are heated with 25 parts of coal and 2 of soda in a current of nitrogen at 1350° for 10–12 hours—

$$4SiO_2+8C+3N_2=2Si_2N_3+8CO$$

The cooled product is decomposed by boiling with a 20-per-cent. solution of caustic soda, or by milk of lime in autoclaves, or by boiling 100 kg. of nitride with a solution of 40 kg. common salt and 2 kg. caustic soda in 400 litres of water.

In the Serpek process, formerly worked in the Savoy, Switzerland, aluminium nitride, AlN, was produced by passing a mixture of bauxite (natural aluminium oxide) and coke through a revolving electric furnace at 1500–1600°—

$$Al_2O_3+3C+N_2=2AlN+3CO$$

The bauxite was calcined in the upper part of the furnace by the hot gases, and the mixture then fell over carbon rods heated electrically and set in the side of the furnace tube. The product withdrawn from the furnace contained 26 per cent. of nitrogen, and could be decomposed by boiling with water under 4–6 atm. pressure, or with weak alkali, with formation of ammonia. The process is no longer worked.

Ammonia from Cyanides.—Since the discovery, early in the nineteenth century, that cyanides are produced when mixtures of alkalies and carbon are heated to whiteness in a current of nitrogen—

$$Na_2CO_3+4C+N_2=2NaCN+3CO$$

and that cyanides are decomposed by steam with production of ammonia—

$$NaCN+2H_2O=HCOONa+NH_3$$

numerous attempts have been made to obtain ammonia from atmospheric nitrogen in this way. All these have so far been unsuccessful, and it would hardly have been necessary to have made reference to the subject but that a recent communication from J. E. Bucher appears once more to have aroused considerable interest in the matter—so much so that a considerable sum of money has been allocated by the American Government for the investigation of the process. A brief account of some of the earlier work may be of interest.

L. Thompson (*Dingl. J.*, **23**, 281, 1839) observed that cyanide is readily produced by heating a mixture of potassium carbonate, charcoal, and iron, in a stream of nitrogen. The presence of iron was found to be essential for the successful working of the process.

Newton in 1840–1843 took out patents for a similar process. Nitrogen was obtained by passing the exit gas from vitriol chambers, which had already had a certain amount of oxygen abstracted in the chamber reactions, through a mixture of ferrous sulphate and lime. This was passed over a mixture of potassium carbonate and charcoal heated to bright redness. The process was worked at Newcastle-on-Tyne for a few years, but failed on account of the great wear and tear on the retorts by the fluxing action of the fused salts.

Ludwig Mond in 1882 tried the process which had been proposed by Margueritte and Sourdeval in 1860. It had been observed that cyanide formation occurred more readily with potassium than with sodium, and most readily with barium, salts. A mixture of barium carbonate and charcoal (formed by briquetting with pitch and sawdust), with or without the addition of iron filings, was heated strongly in a fireclay retort, when a porous mass of barium oxide with excess of carbon resulted —

$$BaCO_3+C=BaO+2CO$$

A slow current of producer-gas, obtained by blowing air through red-hot coke, and consisting of nitrogen and carbon monoxide, was then passed over this mass, heated to 1400° C. in vertical retorts, until a sufficient amount of nitrogen was absorbed—

$$BaO+3C+N_2=Ba(CN)_2+CO$$

The material was then cooled to 500° C. by a current of cold producer-gas, and steam blown through at this temperature, when ammonia was evolved—

$$Ba(CN)_2+4H_2O=2NH_3+Ba(COOH)_2$$

The intermediate reactions leading to the formation of cyanide, discovered much later by Frank and Caro, have been described on p. 203.

The process did not pay, and was abandoned by Mond, who afterwards turned his attention to the recovery of ammonia in the gasification of coal (p. 187).

Various other processes have from time to time been tried, but have been abandoned.

Bucher (*J. Ind. Eng. Chem.*, **9**, 233, 1917) claims that nitrogen can be fixed in the form of sodium cyanide by heating an intimate mixture of equal weights of sodium carbonate, coke, and iron, made into briquettes, to 900°–950° in a stream of producer-gas ($CO+N_2$). The resulting product is stated to contain up to 20 per cent. of sodium cyanide, which is decomposed by steam with production of ammonia—

(i) $Na_2CO_3+4C+N_2=2NaCN+3CO—138{\cdot}5$ kg. cals.
(ii) $NaCN+2H_2O=HCOONa+NH_3$

Bucher's claim that previous workers have failed because they omitted to add iron, which catalyzes the reaction so that fixation of nitrogen proceeds at a comparatively low temperature, is not in accordance with the facts, because the use of iron, as well as of nickel and manganese as catalysts has been mentioned in former patents; *e.g.* Margueritte and Sourdeval, Brit. Pat. 1027 of 1860. It may be that the previous experiments were carried out at too high a temperature, and it is certainly a matter of importance to try whether Bucher's proposal will lead to a satisfactory method for the production of ammonia on a large scale. If the method succeeds, it will doubtless replace all the other synthetic processes, on account of its simplicity and cheapness.

Synthetic Ammonia: the Haber Process.—After earlier unsuccessful attempts to bring about the union of hydrogen and nitrogen to an appreciable extent, dating from the observation of Regnault about 1840 that a mixture of one volume of nitrogen and three volumes of hydrogen when sparked in a eudiometer over sulphuric acid gradually disappeared and was converted into ammonium sulphate, the problem was solved by the researches of Haber and his pupils, commencing in 1905, and in 1910 the technical process was begun in Germany by the Badische firm.

Haber found that the equilibrium—

$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

is reached with increasing concentrations of ammonia at high pressures and moderately low temperatures as follows:—

Pressure in atm.	Per cent. NH_3 in equilibrium mixture N_2+3H_2 at different temperatures.				
	550°	650°	750°	850°	950°
1	0·077	0·032	0·016	0·009	0·005
100	6·71	3·02	1·54	0·874	0·542
200	11·9	5·71	2·99	1·68	1·07

The problem, therefore, was to find a catalyst which accelerates the reaction velocity to such an extent at a sufficiently low temperature that the yield of ammonia is sufficient to make the process workable on a technical scale. The conditions obtaining are exactly analogous to those discussed in connection with the contact process and the preparation of chlorine by the method of Deacon (cf. pp. 45, 119). Numerous catalysts have been patented in connection with the Haber process; among them are preparations containing cerium, manganese, tungsten, uranium, ruthenium, osmium, and especially catalysts mixed with smaller quantities of other materials which act in such a way as to produce a more efficient catalyst from a less efficient—the so-called "promoters." Such a catalyst, for instance, is a mixture of iron and molybdenum.

Plant for the annual production of 30,000–60,000 tons of ammonia by the Haber process (as sulphate) was said to be in operation in Germany at the outbreak of war at a single works at Oppau, and the total production in 1916 by the Haber process has been given as 500,000 tons ammonium sulphate, at a cost of £6 per ton. These figures are probably fallacious, although Germany has had many years' start over other countries in experimental work on the synthetic ammonia process. The operation of the process, which involves the use of hydrogen compressed to 100–200 atm. at a temperature of about 500°, must call for considerable experience and skill, which may have been acquired by the Badische company, but could hardly be gained elsewhere in time to make the process useful as a war proposition. The cyanamide process is much simpler than the Haber process, the plant could be erected in a much shorter time, and the control necessary could be more easily obtained under the present conditions than is the case with the synthetic method. The ammonia produced in Germany is required for the preparation of nitric acid by oxidation (see next section).

Comparison of Nitrogen Fixation Processes.—From the various sources of published information the following tables have been drawn up, in which the power requirements are given, together with the approximate costs, for the fixation of a unit of nitrogen in the various processes already discussed. In these calculations, and those in the table on p. 169, the following equivalents have been adopted:—

1 year=8750 hours ; 1 metric ton=1000 kg.=2205 lbs. ; 1 kilogram calorie=0·001165 K.W.H. ; 1 ton average coal=0·0925 K.W. year ; 1 dollar= 4·183 shillings ; 1 K.W. year=1·360 H.P. year ; 1 kg. cal.=3·968 B.Th.U.

It will be seen that, apart from the figures relating to the Haber process and one or two isolated estimates under other heads, there is fair agreement among the various

Process.	Grams N fixed per K.W.H.	K.W.H. per kg. N fixed.	K.W. years per ton N fixed.	H.P. years per ton N fixed.
I. ARC PROCESS.				
Birkeland and Eyde (1·25 per cent. NO)	15·7	63·7	7·26	9·87
Schönherr (1·5 per cent. NO)	16·7	59·8	6·815	9·27
Pauling (1·5 per cent. NO)	16·7	59·8	6·815	9·27
II. HAÜSSER PROCESS	5·56	180	20·45	27·8
III. CYANAMIDE (20 per cent. N).				
Baur	56·8	17·6	2·0	2·72
Haber	50·0	20·0	2·276	3·095
Lunge	56·8	17·6	2·0	2·72
Summers	60·3	16·6	1·89	2·57
Landis	56·4	17·75	2·02	2·75
Kroczek	39·0	25·7	2·925	3·97
IV. HABER SYNTHETIC.				
Lunge (not including compression and preparation of gases)	680	1·47	0·1673	0·2275
——	38	26·35	3	4·08
Washburn	28·2	8·88	1·01	1·38
Landis	28·2	8·88	1·01	1·38
Summers (not including preparation, purification and compression of gases, and refrigeration of ammonia)	66·7	1·5	0·171	0·233
V. SERPEK PROCESS (25 per cent. nitride).				
Norton	56·9	17·6	2·01	2·725
Serpek	85·5	11·7	1·33	1·808
Kroczek	80·3	12·5	1·42	1·93
Lunge	113·8	8·8	1·00	1·365
Summers (apart from coal)	83·25	12·0	1·368	1·86
——	57·0	17·55	2·0	2·72

statements. As far as one can judge, after taking all the facts into consideration, the following table of power-consumption will probably not be far from the truth :—

Process.	Grams N fixed per K.W.H.	K.W.H. per kg. N fixed.	K.W. years per ton N fixed.	H.P. years per ton N fixed.
Birkeland-Eyde arc	15·7	63·7	7·26	9·87
Modern arc	16·7	59·8	6·815	9·27
Haüsser	5·56	180	20·45	27·8
Cyanamide	50	20	2·276	3·095
Haber	28	8·9	1·03	1·40
Serpek	80·3	12·5	1·42	1·93

Costs of Nitrogen Fixation.—The cost of a unit of nitrogen fixed in any of the processes described will depend on the three considerations—

(1) The cost of the raw materials.

(2) The cost of the power.

(3) The working costs, apart from power, including capital charges.

The Arc Process.—In the fixation of nitrogen by the arc, the only raw materials used are atmospheric air and water. Both of these exist in abundance, and the only costs which need be considered are power and working costs. The power costs have been summarized on the table on p. 169, and these figures together with the power consumption on p. 212 enable one to make an approximate estimate of the cost of nitric acid produced by the arc.

In the Birkeland-Eyde process, 15·7 grams N are fixed by 1 K.W.H. Taking the price of power at 0·0238*d.* per K.W.H. at Notodden, we find that one kilogram of nitrogen is fixed for a power cost of 1·516*d.* The power cost for 1 ton HNO_3 as weak acid is therefore £1·403. The corresponding power costs for the Schönherr and Pauling furnaces would be, taking power at 0·0269*d.* per K.W.H. at Milan (where the improved Pauling furnace is in use), £1·491.

According to Flusin (*Chem. Ind.*, 1914, p. 525), the working expenses of an arc plant amount to £2 2*s.* to £2 8*s.* per ton HNO_3 as tower acid per annum. The mean, £2·5 per ton, appears to be a reasonable figure.

The capital cost for an installation producing nitric acid by the arc process is a somewhat speculative figure. Washburn ("The Facts in the Nitrogen Case," 1916) gives the installation cost at £93 per ton HNO_3 per annum, which is certainly much too high. An estimate of the Norwegian costs may be derived from the figures given for the Rjukan works, which are stated to employ 280,000 H.P., and to represent a capital of £3,300,000 (Lunge, "Sulphuric Acid," Suppl. to vol. i., p. 109). Taking the figure of 9·87 H.P. years per ton N fixed (p. 212), we find that the capital cost per ton HNO_3 as weak acid amounts to about £26, which includes the cost of the furnace installation, absorption towers, etc., the power houses with reservoirs, etc.

According to K. Scott (*J. Roy. Soc. Arts*, **60**, 646, 735, 1912) the cost of the Norwegian plant is £4·8 per K.W., which is equivalent to a capital cost of £35 per ton HNO_3 per year. The mean of these two estimates, viz. £30 per ton, may for the present be taken as approximately correct. No reliable figures for installations other than those using water power are available (cf., however, K. Scott, *Chem. News*, **116**, 187, 1917).

It appears that the interest and amortization on the capital costs are already included in the figures for power-costs and working costs stated above, so that no further addition is necessary in order to find the total production costs.

In the following table a working cost of £2·5 per ton HNO_3 has been added to the power costs to give the total costs in the last column :—

Process.	Gram N fixed by 1 K.W.H.	Cost of 1 K.W. year in £.	Cost of power per kg. N fixed in pence.	Cost of power per ton HNO_3 in £.	Total cost per ton HNO_3 as 50 per cent. acid in £.
Birkeland Eyde Arc ..	15·7	0·904*	1·58	1·465	3·956
		1·0	1·75	1·622	4·122
		1·25	2·19	2·03	4·53
		2·0	3·50	3·245	5·745
		3·0	5·25	4·86	7·36
		3·75	6·57	6·08	8·58
Schönherr or Pauling Arc	16·7	1·00†	1·643	1·52	4·02
		1·25	2·055	1·905	4·405
		2·0	3·286	3·05	5·55
		3·0	4·929	4·57	7·07
		3·75	6·16	5·71	8·21

* At Notodden. † At Milan.

To these figures must be added the cost of concentrating the weak acid from the absorption towers, which will be shown later to amount to about £3 per ton (50 per cent. acid to 97 per cent. acid).

Cyanamide.—The cost of production of cyanamide containing 20 per cent. N by the discontinuous process is stated to be as follows, per lb. N fixed :—

At Odda ..	.. 2·75*d.*
In Italy ..	.. 2·43*d.*

These costs refer to power at £0·554 and £1 per K.W. year, respectively. The corresponding costs of 1 ton NH_3 *in the form of cyanamide*, are £21·14 and £18·68, respectively.

According to Landis the total cost of production of ammonia from cyanamide, including power, steam, labour, repairs, interest, depreciation, etc., amounts to £4·24 per ton, with cyanamide delivered at the works. The total cost per ton of ammonia as such, with cyanamide at the prices given above, would thus be £25·38, and £22·92, respectively. With a works making carbide, cyanamide and ammonia, the cost per ton of ammonia by the discontinuous process would therefore amount to about £25, assuming the low power costs of £0·554 (Odda) and £1 (Milan) per K.W. year, respectively. In most cases, however, the power costs would presumably be greater than these, and an estimate for the cost of production of cyanamide with power at different costs is given below.

For the production of 1 ton cyanamide (20 per cent. N) the costs will be as follows, exclusive of power :—

	£
0·76 ton lime at £0·75 per ton	0·570
0·50 ton anthracite at £1 per ton ..	0·500
0·435 ton nitrogen at £0·933	0·410
Electrodes	0·100
Labour	0·650
General expenses	1·140
	3·370

Power required per ton cyanamide=0·404 K.W. year. With a 95-per-cent. efficiency, the weight of cyanamide for 1 ton NH_3 will be 4·32 tons.

The cost of materials, etc., for the preparation of this, exclusive of power, is 4·32 × £3·37 = £14·55.

The cost of conversion of the cyanamide to ammonia is £4·24 per ton NH_3.

∴ total cost of 1 ton NH_3 exclusive of power=£18·79

The power required per ton NH_3=0·404×4·32=1·745 K.W. year.

The costs of power, with various prices per K.W. year, will be as follows :—

	£	£	£	£	£
Power per K.W. year ..	0·554	1·0	2·0	3·0	3·75
Power cost	0·967	1·745	3·49	5·235	6·55
Cost of 1 ton NH_3 ..	19·76	20·54	22·28	24·03	25·34

The corresponding costs for the continuous cyanamide process are not published; they probably amount to about 80 per cent. of those given above. These costs would then be as follows :—

	£	£	£	£	£
Power per K.W. year ..	0·554	1·00	2·0	3·0	3·75
Cost per 1 ton NH_3 ..	15·8	16·40	17·80	19·2	20·25

Serpek Process.—According to Donath and Indra, the cost of 1 ton ammonia produced by the Serpek process is £11 3*s.* 3*d.* Norton states that the cost of fixation of nitrogen alone by the Serpek process is 2·65*d.* per lb. The selling price of Serpek's nitride (26 per cent. N) in France in 1911 was 3·25*d.* per lb. If we adopt 2·65*d.* per lb. for 26 per cent. nitride as a minimum figure, the cost of 1 ton ammonia, *still in the form of nitride,* is £8·016. The cost of production of ammonia from the nitride is stated by the same authority to be such that ammonium sulphate may be produced at 3·5*d.* per lb. This works out at £8·414 per ton of ammonia, which appears to be too small. As the Serpek works are now shut down, it hardly seems worth while to make more detailed calculations.

Haber Synthetic Process.—The cost of ammonia produced by the Haber process is still very problematical. Apart from an estimated cost given by Haber, and another conjectured by Maxted, both on the basis of small-scale experiments, there is no published information on the subject.

Haber's estimate is £12 10s. per ton ammonia; Maxted has given the figure at £10–£12 per ton. These figures are undoubtedly too low; other unpublished estimates reach as high as £22 per ton, but it is possible that £15 per ton is the minimum probable figure as far as can be judged by small-scale working.

The cost of ammonia made by the Haber process depends, apart from the power costs, on the prices of hydrogen and nitrogen. Some figures for these are given below (pre-war).

Cost of nitrogen—

In France, 0·09–0·45*d*. per lb.
In Germany, 0·16*d*. per lb.
From small Linde Plant, 0·324*d*. per lb.

Cost of hydrogen—

Griesheim and Bitterfeld works (from water-gas), 6*d*. per lb.
Oerlikon (electrolytic), 4·5*d*. per lb. for electric current alone, viz. about 6*d*. per lb. hydrogen.
German electrolytic, 7·2*d*. per lb.
Ditto compressed to 150 atm. in cylinders, 22·4*d*. per lb.
Haber (estimated), 5·50*d*. per lb.

The cost of materials is therefore about as follows:—

14 lbs. nitrogen at 0·25*d*. per lb. .. = 3·5*d*.
3 lbs. hydrogen at 6*d*. per lb. .. = 18·0*d*.

∴ cost of materials for 17 lbs. ammonia = 21·5*d*.

∴ cost of materials per ton ammonia .. = £11·75

The power required is about 1·03 K.W. years per ton N (p. 212), hence for the fixation of 1845 lbs. N in the form of 1 ton of ammonia, about 0·85 K.W. year would be absorbed. At a cost of £9 per K.W. year this would bring the power cost to £7·65, so that the total cost of production of 1 ton of ammonia by the Haber process would amount to £11·75 + £7·65 = £19·4, which is about £4 in excess of the figure of £15 per ton adopted above. The difference is accounted for by the price of hydrogen adopted above, viz. 6*d*. per lb., which is probably higher than the minimum cost (Haber's figure of 5·5*d*. per lb. is probably a conservative estimate for modern plants), and the price of power, which may conceivably be reduced below £9 per K.W. year, this being the lowest pre-war price for steam- or gas-generated electric power in England.

By-product Ammonia.—The figures given above may be compared with those for by-product ammonia obtained from gas-works, coke-ovens, or blast furnaces. This ammonia appears almost exclusively on the market in the form of ammonium sulphate, and the price of this product has been largely regulated by that prevailing for Chili nitre. The average pre-war price of ammonia in the form of by-product sulphate, for several years, was £55·33 per ton NH_3 in the form of sulphate. To arrive at the market value of ammonia in the form of crude liquor, certain deductions have to be made from this figure, viz. 3·5 per cent. of the price of the sulphate representing brokerage and commission for marketing, and £3 per ton for the cost of converting into sulphate, including the cost of acid, labour, and packing. The balance then represents the value of the ammonia in 1 ton 25 per cent. sulphate, viz. 0·25 ton NH_3 in the form of crude liquor. The above figure then represents £41·40 per ton NH_3 as crude liquor, which is of the order of £40·46 per ton, obtained from the average price of 14*s*. per ton for crude 8 oz. liquor delivered.

The lowest pre-war market price for sulphate was £7·5 per ton, which corresponds to £16·96 per ton NH_3 in the form of crude liquor.

The price of concentrated gas liquor (14–17 per cent. NH_3) was about 9*s*. 3*d*. per 1 per cent. NH_3, or £46·25 per ton NH_3 in the form of 16 per cent. liquor.

Purified ammonia spirit (20–25 per cent. NH_3) cost about 10*s*. 3*d*. per 1 per cent. NH_3 per ton at the works, which corresponds to £51·25 per ton NH_3 in the form of pure liquor.

These prices, however, do not represent in any way the real cost of by-product ammonia, and in the case where the ammonia is utilized at the works itself, say for oxidation to nitric acid, the cost would be considerably less. The actual cost of recovery ammonia at the works, including purification, probably amounts to less than £10 per ton, which is less than that of synthetic ammonia. The advantage to such works of utilizing their ammonia for oxidation is therefore evident. The supply of by-product ammonia is, however, limited, and this source alone would probably not be sufficient to produce the nitric acid required, in addition to the ammonium sulphate needed for various processes, such as the ammonia-soda process, and for agriculture.

Cost of Production of Ammonium Sulphate from Gas Liquor.

(1) *Direct Fired Still, old type.*—

Fuel consumption: 1 cwt. coal per ton of gas liquor treated.

Lime used: 15–20 per cent. of the weight of the ammonium sulphate obtained.

Labour: 2 men for dealing with 10 tons of liquor per day.

Capacity: 10 tons of 2¼ per cent. liquor, *i.e.* 0·7 ton of sulphate per day.

The apparatus is about 10 ft. high and 5 ft. wide; the column and lime vessel add another 5 ft. to the height.

Cost with sulphate apparatus, £175.

Cost of Production of 1 ton Ammonium Sulphate.

	Tons.	Price.	£	s.	d.
Sulphuric acid, 148° Tw.	1·06	40*s.*	2	2	5
Lime (18 per cent. of sulphate obtained)	0·18	12*s.* 6*d.*		2	3
Coal	0·715	8*s.*		5	9
Gas liquor	14·3	12*s.*	8	12	0
Casks and packing				8	0
Labour, two men at 4*s.* per day				11	5
Sundries, repairs, etc.				6	8
Amortization on plant, £175, buildings £100; total £275		10 per cent.		2	3
Interest on plant and buildings, £275, and land £75; total £350		5 per cent.		1	5
Total per ton sulphate			£12	12	2

(2) *Feldman Still.*—7½–8 tons of liquor per day.

	Tons.	Price.	£	s.	d.
Sulphuric acid, 168° Tw.	0·74	£4	2	19	7
Lime				3	0
Coke				9	0
Gas liquor	14·3	12*s.*	8	12	0
Wages at 4*s.* 3*d.* per day				8	0
Sundries				3	0
Interest and amortization				5	0
Total per ton sulphate			£12	19	7

(3) *Grüneberg and Blum Still.*—3500 tons liquor of 5¼° Tw. per annum (from 35,000 tons of coal carbonized). Annual costs :—

	Tons.	Price.	£	s.	d.
Sulphuric acid, 142° Tw.	389	£2	778	0	0
Lime	71	12*s.* 6*d.*	44	7	6
Coal	175	8*s.*	70	0	0
Gas liquor, 5¼° Tw.	3500	12*s.*	2100	0	0
Casks and packing			155	12	0
Sundries, repairs, etc.			116	14	0
Labour, four men for 50 weeks		25*s.*	250	0	0
Depreciation of plant, £300; buildings, £150; total £450		10 per cent.	45	0	0
Interest on plant, and buildings, £450; land, £100; total £550		5 per cent.	27	10	0
Total for 389 tons sulphate			£3587	3	6
Cost per ton sulphate			£9	4	8

The cost of manufacturing ammonia solution by direct distillation will depend on the concentration and purity of the solution obtained. The cost of production of 1 ton of ammonium sulphate, £9 4*s.* 8*d.*, less the cost of sulphuric acid, and packing, leaves about £6·75 as the cost of ammonia corresponding with 1 ton sulphate, or £26 per ton ammonia. The cost at the works where the ammoniacal liquor is produced is much less, since the cost of condensing the ammoniacal liquor cannot be as much as 12*s.* per ton. The cost of extra purification, when pure ammonia liquor is to be obtained, is not very definitely known; it probably amounts to about £7 per ton of ammonia.

TABLE OF COSTS OF NITROGEN FIXATION.

Process.	Raw product.	Cost of power per K.W.Y., in £.	Cost per ton N in raw produot, in £.	Cost per ton NH_3 as such, in £.	Cost per ton HNO_3 as 50 per cent. acid, in £.	Cost per ton HNO_3 as 97 per cent. acid, in £.
Birkland Eyde arc	30 per cent. nitric acid.	0·904	17·85	—	3·965	6·97
		1·0	18·55	—	4·122	7·12
		1·25	20·35	—	4·53	7·53
		2·0	25·85	—	5·745	8·75
		3·0	33·10	—	7·36	10·36
		3·75	38·6	—	8·58	11·58
Schönberr and Pauling arcs	30 per cent. nitric acid.	1·00	18·1	—	4·02	7·02
		1·25	19·8	—	4·405	7·41
		2·0	25·0	—	5·55	8·55
		3·0	31·8	—	7·07	10·07
		3·75	36·9	—	8·21	11·21
Discontinuous cyanamide ..	Cyanamide, 20 per cent. N.	0·554	17·6	19·76	9·58	12·58 *
		1·0	19·8	20·54	9·85	12·85 *
		2·0	21·85	22·28	10·43	13·43 *
		3·0	24·05	24·03	11·01	14·01 *
		3·75	25·6	25·34	11·45	14·45 *
Continuous cyanamide ..	Cyanamide, 20 per cent. N.	0·554	14·1	15·8	8·27	11·27 *
		1·0	14·8	16·4	8·47	11·47 *
		2·0	16·5	17·8	8·93	11·93 *
		3·0	18·0	19·2	9·40	12·40 *
		3·75	20·6	20·25	9·75	12·75 *
Serpek	Aluminium nitride, 26 per cent. N.	—	9·73	8·414	5·80	8·80 *
Haber	Pure NH_3.	—	18·2	15·0	8·0	11·00 *

* With 90 per cent. overall efficiency on oxidation and absorption; for calculation see p. 259.

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SECTION IX.—THE OXIDATION OF AMMONIA

The Oxidation of Ammonia.—It has been known since the time of Kuhlmann (1839) that when a mixture of air and ammonia gas is passed over heated spongy platinum, or certain catalytic materials, oxidation occurs, not to nitrogen and water, which are the chief products of the combustion of ammonia in oxygen, but to red fumes of oxides of nitrogen. Kuhlmann formulated the reaction as follows :—

$$2NH_3+7O=N_2O_4+3H_2O$$

Although this reaction was the basis of a well-known lecture experiment (cf. for instance, Mendeléeff, "Principles of Chemistry," i. 283), and was known to nearly all chemists, it was not thought of as a technical possibility until about 1871, when Tessié du Motay took out a patent for oxidizing a mixture of air and ammonia by passing over chromates, manganates, and plumbites, heated to 300°–500°, afterwards injecting steam to produce nitric acid from the oxides of nitrogen. The first impetus to recent technical applications was given by the experiments of Ostwald and Brauer, begun in 1900 and leading to the patents of 1902. For this reason, the process for the catalytic oxidation of ammonia is often called the Ostwald process, although, as has just been stated, a patent for ammonia oxidation was taken out as early as 1871, and the German patents were not granted to Ostwald on account of the previous work of Kuhlmann. Ostwald and Brauer found that the yield of oxides of nitrogen in Kuhlmann's experiment as usually performed was poor ; most of the ammonia is burnt directly to nitrogen and steam. Ostwald had, just about that time, formulated the Law of Successive Reactions, according to which a system of reacting substances does not pass over directly into the most stable system of products, but into the next less stable, or the least stable of all the possible states. Thus, when chlorine is passed into caustic soda solution, the reaction is not the formation of sodium chloride and oxygen, which are the ultimately stable products, but instead the various oxy-compounds $NaClO$, $NaClO_3$, $NaClO_4$ are produced under various conditions. All these are unstable under their conditions of formation. Now it is known (cf. p. 39) that a chemical reaction is always accompanied, when it occurs spontaneously, by a fall in the available energy of the system, and the law just formulated is therefore equivalent to the statement that the available energy of a system undergoing chemical change does not at once fall to its lowest level, but does so in stages somewhat as the potential energy of a ball rolling down a staircase drops in stages, and the ball may even require an impulse at each step to carry it to the next one. There is therefore, a certain reluctance to proceed to dissipation of energy, although the latter is inexorably demanded by the second law of thermodynamics for every material change; seen in this light the law of successive reactions bears some relation to the Principle of Least Action of Le Chatelier (see Partington, "Thermodynamics," p. 304). The formation of oxides of nitrogen in the oxidation of ammonia must be regarded as an unstable intermediate phase of the reaction, and it occurred to Ostwald that if these oxides could be removed very rapidly from the sphere of chemical activity of the catalyst, so that the time of contact is very small, they might be preserved from further decomposition. This in fact was found to be the case when the time of contact did not exceed 1/100th of a second. The intermediate product—

$$2NH_3 \rightarrow 2NO \rightarrow N_2$$

in the series of reactions—

$$\begin{aligned} &\text{(i)} & 4NH_3+5O_2&=4NO+6H_2O \\ &\text{(ii)} & 4NO&=2N_2+2O_2 \\ &\text{(iii)} & 6NO+4NH_3&=6H_2O+5N_2 \end{aligned}$$

was thus isolated.

At the temperature of oxidation the only oxide of nitrogen which could exist is nitric oxide, NO, and the gases from the hot catalyst are in fact colourless and only become red on cooling down to about 200°. Equation (i) above, therefore, expresses the primary reaction in the oxidation of ammonia.

But nitric oxide is unstable below a certain temperature, and tends to split up into oxygen and nitrogen. The velocity of decomposition is very much accelerated by rise of temperature (see p. 165); below a temperature of about 1200° it is so slow that NO is practically stable. Hence the NO produced in the oxidation must be removed quickly from the catalyst and cooled.

As a result of Ostwald and Brauer's work, a small factory was erected at Gerthe, near Bochum in Westphalia, for the oxidation of coal-tar ammonia, with a monthly production of 130 tons of ammonium nitrate. The Ostwald patents were then taken over and exploited by the Nitrogen Products and Carbide Co., who have erected works in Belgium and France, and in England at Dagenham Dock, on the Ostwald principle. Recently many new developments of the process have been made, and these will be described, together with the old process worked by the Nitrogen Products Co., which might be called the Ostwald process.

It has been suggested (Mendeléeff, "Principles of Chemistry," i. chap. 6) that the oxidation of ammonia takes place by successive hydroxylation and splitting off of water:

(1) $2NH_3+O_2=NH_2(OH)+H_2O$, hydroxylamine.
(2) $2NH_2OH+O_2=NH(OH)_2+H_2O$, dihydroxyammonia.
(3) $2NH(OH)_2+O_2=2N(OH)_3+H_2O$, orthonitrous acid.
(4) $2N(OH)_3=N_2O_3+3H_2O$, nitrous anhydride.
(5) $2N_2O_3=4NO+O_2$.

The oxidation part of the series of reactions stops at the stage where N_2O_3 is produced, and on this hypothesis it would appear probable that the best yield would be got when the air and ammonia were mixed in the proportions to form N_2O_3. Although these proportions are in fact very suitable, no very marked difference in the yield is noticed even if the proportions of air and ammonia are varied within fairly wide limits, provided more than enough air is added to form NO. In actual working the result depends on the rate of passage of the gas through the catalyst; for relatively slow flow rates (0·01 sec. contact) the results are better, as Ostwald discovered, with sufficient air to form NO_2, but with higher flow rates (0·001 sec. contact, and less) the proportions for N_2O_3 appear to be most suitable, although the yield is practically the same even if more air is added.

From the equation $4NH_3+5O_2=4NO+6H_2O$ the following proportions follow :—

For NO : 1 vol. ammonia+6·25 vols. air ;
For N_2O_3 : 1 vol. ammonia+7·5 vols. air ;
For NO_2 : 1 vol. ammonia+8·75 vols. air ;
For N_2O_5 : 1 vol. ammonia+10·0 vols. air.

Besides platinum, many other substances can be used as catalytic materials, but the process must then be conducted at higher temperatures. Other catalysts are metallic oxides, especially mixtures, such as a mixture of oxides of iron, cerium, and bismuth; or oxy-salts such as plumbites or plumbates of calcium, zinc or magnesium. The catalysts appear to act as carriers of oxygen in a cyclic action, being themselves alternately oxidized and reduced :—

(1) $RO_m+nO=RO_{m+n}$ (with metals, *e.g.* platinum, $m=0$);
(2) $5RO_{m+n}+4nNH_3=5RO_m+4nNO+6nH_2O$.

From a consideration of the equilibrium data of the reactions :—

$$(1)\ N_2+3H_2 \rightleftarrows 2NH_3$$
$$(2)\ N_2+O_2 \rightleftarrows 2NO$$
$$(3)\ 2H_2+O_2 \rightleftarrows 2H_2O$$

it is possible to deduce the value of the equilibrium constant for the reaction—

$$4NH_3+5O_2 \rightleftarrows 4NO+6H_2O$$

which is assumed to be reversible in the presence of the catalyst; for if—

$$K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_2 = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_3 = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

then $$K = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5} = \frac{K_2^2 . K_3^3}{K_1^2}$$

If therefore the values of K_1, K_2, and K_3 are known for any temperature, the value of K, the equilibrium constant of the ammonia oxidation, is also known for that temperature.

The values of K_1, K_2, K_3 for all temperatures are, however, given approximately by the equations—

$$\log K_1' = \log \frac{p^2_{NH_3}}{p_{N_2} . p^3_{H_2}} = \frac{5775}{T} - 12{\cdot}268$$

$$\log K_2' = \log \frac{p^2_{NO}}{p_{N_2} . p_{O_2}} = -\frac{9450}{T} + 2$$

$$\log K_3' = \log \frac{p^2_{H_2O}}{p^2_{H_2} . p_{O_2}} = \frac{24910}{T} + 1{\cdot}2$$

Hence $$\log K' = 2 \log K_2' + 3 \log K_3' - 2 \log K_1'$$

$$= \frac{2 \times (-9450) + 3 \times 24910 - 2 \times 5775}{T}$$

$$+ 4 + 3{\cdot}6 + 24{\cdot}536$$

$$\therefore \log K' = \frac{44280}{T} + 32{\cdot}14$$

It follows that, even for very large values of T, the expression log K′ has considerable positive values. The equilibrium

$$4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O$$

if attained, will be in the sense that the substances on the right of the equation are practically completely formed from the initial substances at all temperatures, *i.e.* the reaction is practically quantitative at all temperatures.

A similar result follows from an application of Nernst's theorem (p. 41).

It appears, therefore, that so far as equilibrium goes, the oxidation of ammonia is practically complete (100 per cent.) at all attainable temperatures. It is, in fact, a result of experiment that the yield is very little influenced by the temperature up to a certain point, but it begins to fall off at very high temperatures (above 1000° C.). This falling off is, however, most probably due to the decomposition of the unstable NO, which becomes appreciable above 1200° C. (cf. p. 165).

It has been shown that the oxidation commences, with platinum as a catalyst, at a dull red heat (550° C.), and proceeds rapidly and practically completely at about 650° C. There is no point in going to higher temperatures, such as 800° (which has been advocated); in fact, the yield falls off slightly at high temperatures. The yield is practically 100 per cent. in laboratory experiments.

The reaction goes equally well with dried or moist gases; the presence of moisture appears to be slightly beneficial.

The conversion of NO to NO_2, and the absorption of NO_2 in water to produce nitric acid, take place as described in connection with the arc process (p. 166).

Apparatus for the Oxidation of Ammonia.—The oxidation of ammonia on a technical scale depends on the solution of the following four problems:—

(1) The production of a supply of ammonia gas of the requisite purity, either alone or mixed with air.

(2) The preparation of a mixture of ammonia and air in the proper proportions for oxidation.

(3) The conversion of this mixture into oxides of nitrogen by passing over a suitable catalyst.

(4) The absorption of the oxides of nitrogen to produce nitric acid.

If strong nitric acid is to be produced from the 50–60 per cent. tower acid obtained in (4), the problem of the concentration of nitric acid must be added. This will be treated generally later on.

Of these problems, the first three are comparatively simple. The preparation and purification of ammonia from by-product ammonia is well known in this country, and the preparation of ammonia by the cyanamide process has also been worked out successfully in England, on the Continent, and in America. The synthetic ammonia from the Haber process is, it is true, not known outside Germany, but the other two sources just mentioned will provide sufficient ammonia for some time to come. The oxidation of ammonia can, as a result of recent work, be carried out very simply with an efficiency approaching 100 per cent. But the production of nitric acid from the oxides of nitrogen is a problem which cannot yet be said to have a satisfactory solution. The absorption in water towers, described on p. 166, is a process which presents no great difficulty, although the theory has been only incompletely made out. The towers are so cumbrous and costly that they can be regarded only as a tentative solution of the problem. At the same time, this side of the question should not be unduly exaggerated. The tower space required is not large when compared with the lead-chamber capacity of the sulphuric acid plants, yet one never hears objections from the users of such chambers, who may be dissatisfied with the tower space required in ammonia oxidation plant. Another fact which should be kept in mind is that the towers already laid down for this purpose are often unduly large and expensive, on account of faulty design. Various attempts have been made to dispense with water absorption, but the fact that a certain amount of reaction space must always be allowed for the reaction—

$$2NO+O_2=2NO_2$$

which is fairly slow with dilute gases, must not be overlooked.

The different stages in the oxidation process will now be considered in more detail.

Preparation of the Ammonia.—There has been some dispute as to the most suitable source of the ammonia for oxidation. The producers of cyanamide have supplied the information that gas-works or by-product ammonia is unsuitable, on account of the readiness with which platinum becomes inactive, or is "poisoned," by the sulphur compounds. It is true that ammonia purified from sulphur is necessary for the process, but such purification is an everyday operation in the manufacture of ammonia, and no special purification is required, beyond perhaps washing the gas with caustic soda solution. Cyanogen, which is usually a powerful poison for platinum when the latter is used as a catalyst, as well as hydrocyanic acid, are readily oxidized to NO by platinum—an observation made in 1839 by Kuhlmann, and recently confirmed by Moldenhauer and Wehrem (*Zeit. angew. Chem.*, 1914, 29, 334)—

$$C_2N_2+3O_2=2NO+2CO_2$$

The organic bases such as pyridine and pyrrol, which are present in by-product ammonia, are removed by washing with oil, and if present in traces would probably not be injurious. Thiophene should be removed, if possible, but is not known to exert any bad effect. Of far greater influence is the presence of dust, especially oxide of iron, in the air or gases supplied to the catalyser, as the platinum then rapidly loses its activity.

The apparatus for the production of ammonia gas from gas liquor is similar to that already described. The crude liquor is mixed in an iron tank with milk of lime, and is then forced by pumps to the top of a dephlegmating column or ammonia still, where it is met by low-pressure steam blown in at the bottom. Ammonia gas is expelled, and if the top of the column is kept cool by water, the gas escapes fairly dry. Moisture has no influence on the oxidation process. The gas is passed through two water coolers to remove excess of moisture, and then through 25 per cent. caustic soda to remove sulphuretted hydrogen, phenol, etc. The gas should then be washed with heavy oil to remove organic bases, and is then stored over water covered with a layer of oil in a small gasholder, which serves as a balancer. Joints may be made with red-lead and oil.

In practice it is better to start with a 25-per-cent.

ammonia liquor prepared in the ordinary way, with purification, as the dephlegmator becomes choked with lime when gas liquor is used directly. The liquor is sent directly to the column, and treated with steam. The liquor may be stored in a tank on the ground, and forced up to a smaller tank 35 ft. above ground, which is connected by an iron pipe to the column; liquor then flows to the latter by gravity, and there is no loss. The soda washers need not be used with purified liquor.

Instead of driving off pure ammonia gas as described, which is afterwards mixed with the requisite volume of air (filtered through slag-wool after water-scrubbing to remove dust), the air may be blown through the ammonia column, and with a constant feed of liquor of known strength a mixture of air and ammonia of any desired composition may thus be made with some economy of steam.

In the larger cyanamide works, the ammonia is purified from phosphine, silicon hydride, and acetylene (all of which act much more injuriously on platinum than the traces of sulphur in purified gas-works ammonia) by washing with strong caustic soda solution. The gas is then stored in a balancing gasholder as described, and passed to a mixing pipe. The mixing apparatus for any type of plant may be quite simple; the air and ammonia are measured with orifice meters, the one for ammonia being lined with vulcanite, and the gases are then led to a small box made of aluminium, with one or two baffles.

If synthetic ammonia from the Haber process were used it could, after filtration, be sent direct to the mixer, as it should already be quite pure.

The essential points in the design of an ammonia producing plant are—

(1) It should work uniformly and with little attention, and should not be liable to stoppage.

(2) It should be economical in steam consumption. This depends on the proper regulation of the temperature in the different parts of the column—hot below and cool above.

(3) It should deliver ammonia at a definite rate, or a mixture of air and ammonia at a constant rate and composition if the second type is used.

All piping after the filters should be of aluminium, stoneware, or glass, not iron or metal from which small particles of oxide are removed, which would poison the platinum.

The Oxidation Apparatus: the Converter.—The apparatus in which the oxidation occurs, called the *converter*, varies with the system used. Since no details of any converter using catalysts other than platinum are available, the description will be confined to the platinum catalyst converters. Of these three types are in use—

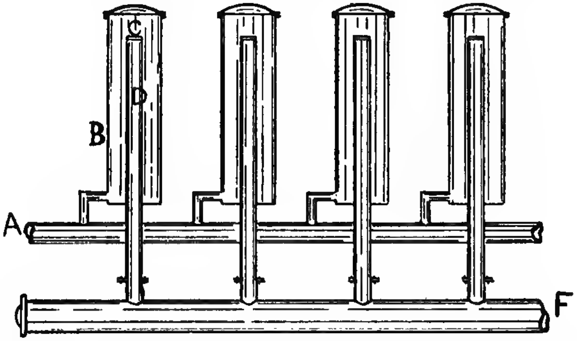

FIG. 56.—Ostwald Ammonia Oxidation Apparatus (Elevation).

A, supply pipe for air and ammonia; B, outer enamelled iron jacket; C, catalyst; D, nickel tube; F, aluminium main to absorption system.

(1) The original type of Ostwald and Brauer, with preheating of the mixture of air and ammonia.

(2) The electrically heated single platinum gauze type, of Frank and Caro.

(3) The Kaiser type, with pre-heated air and multiple platinum gauzes.

(1) *The Ostwald-Brauer Converter.*—This type of converter (Fig. 56) has been mainly exploited by the Nitrogen Products Co., and consists of a nickel tube, D, about 8 ft. long and 2 in. in diameter, surmounted by about 50 grams

of platinum, C, in the form of a roll of foil, about 2 cm. wide, and surrounded by an outer tube, B, of enamelled iron with an inlet for the air and ammonia mixture at the bottom. A large number of these converters are connected (usually 30 in a battery) through the bottom of the nickel tubes, with a trunk main, F, of aluminium (Fig. 57), passing to the absorption towers. The reaction is started by playing a hydrogen flame over the platinum, and then proceeds without further heating, since the hot gases, composed of oxides of nitrogen and steam, from the catalyst pass down the nickel tube on the inside and heat the mixture of air and ammonia passing up over the outer surface of the nickel on its way to the platinum. The output of such a unit is stated to be 30 tons of HNO_3 per annum. The efficiency claimed is 98 per cent., although this appears to be based on the experiments of Ostwald and Brauer, and the yields in actual works using this type of converter have probably never attained this figure. The output per unit is small, and the method of preheating the gas limits the composition of the mixture to about 9 per cent. of ammonia by volume. With richer mixtures the platinum gets too hot, and with weaker mixtures the heat interchange is not sufficient to promote the oxidation. The nickel is expensive, and not easy to obtain in the form of solid-drawn tubes, but no other metal can be used at the temperature of 600°-800° attained in the converter. A very good quality of chemical enamel is required for the lining of the outer tube. This old system, which is still used by the Nitrogen Products

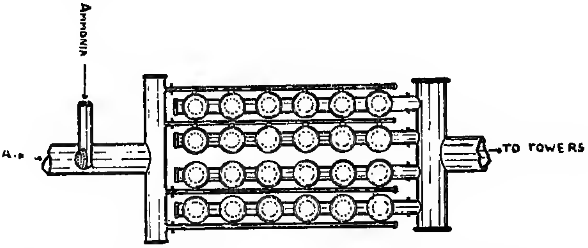

FIG. 57.—Ostwald Ammonia Oxidation Apparatus (Plan).

Co., has therefore many disadvantages. The most serious defects are the difficulty of regulating the temperature, the use of nickel, the large quantity of platinum required compared with modern apparatus, and the small output of each unit.

(2) *The Frank and Caro Converter.*—In this type (Fig. 58) the catalyst is a single layer of fine platinum gauze, D, woven of wire 0·065 mm. diameter with 80 rectangular meshes to the linear inch. This is supported between silver leads, and is heated electrically to about 650°. The gauze is rectangular in shape, 40 cm. by 60 cm., and is supported in an aluminium frame, surmounted by an aluminium cone, E, with a mica inspection window, and a bent tube, also of aluminium, above for carrying off the gas produced by oxidation. Underneath the catalyst is an aluminium box, C, with baffles to promote uniform flow of the air and ammonia mixture passing to the gauze. The lower box is water cooled. The unit is said to be capable of oxidizing 80 kg. ammonia per 24 hours, *i.e.* 300 grams per sq. cm. per 24 hours. The weight of the platinum is about 90 grams, so that the output per gram of platinum is much larger

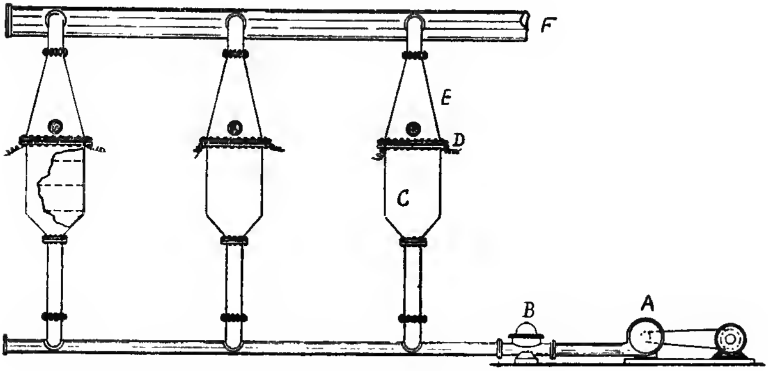

FIG. 58.—Frank and Caro Ammonia Oxidation Apparatus.

A, fan; B, mixer for air and ammonia; C, converter base; D, electrically heated platinum gauze catalyst; E, converter hood; F, main for oxides of nitrogen.

than with the old Ostwald type. The efficiency is given as 90–92 per cent. The apparatus is made by the Bamag firm in Germany, who state that they have supplied more than 30 such plants for the oxidation of 12,000,000 kg. ammonia per annum, and had additional plants under construction in 1916 for the oxidation of 17,000,000 kg. ammonia.

A similar type of apparatus has been specified in the patents of the American Cyanamide Co., but the platinum net used is 2 sq. ft. instead of 3 sq. ft. as in the Frank and Caro type. It is probable that a still more convenient unit would be 1 sq. ft. of net.

A small converter for supplying oxides of nitrogen to vitriol chambers has been described by Schüphaus (see below).

(3) *The Kaiser Converter.*—Dr. Kaiser, of Spandau, introduced in 1910 several modifications in the platinum converter for the oxidation of ammonia. These had their origin in a very dubious theory advocated by Kaiser, to the effect that if the air were preheated to about 300°, or exposed to a spark discharge, before mixing it with the ammonia, the atmospheric nitrogen became in some way "activated," so that when the oxidation of the ammonia occurred on the platinum catalyst, not only was the ammonia practically all converted into oxides of nitrogen, but also a considerable amount of the atmospheric nitrogen was oxidized at the same time, so that the efficiency sometimes reached over 200 per cent., and could usually be about 120 per cent. There is very little doubt that this claim to "autoxidation" of atmospheric nitrogen was based on faulty analytical methods, because no subsequent workers who have made use of methods beyond suspicion have been able to discover any trace of autoxidation. At the same time, Kaiser's plant presented several novel features, which have been the basis of the modern apparatus for ammonia oxidation.

In Kaiser's original apparatus (Fig. 59), several platinum gauzes, D, were used, placed close together across a tube, A, and the air was preheated separately in a coke-furnace to 300°, before mixing with the ammonia 50 cm. in front of the catalyst. Four nets of platinum or platinum-iridium wire, 0·06 mm. diameter, having 80 meshes to the linear inch, were used, placed together in a total thickness of 0·5–0·6 mm. across a silica tube of not less than 10 cm. diameter. The gas velocity was 1 metre per second, giving a time of contact with the catalyst of only 0·0006 sec. In this way, by preheating the air, using several catalytic gauzes very close together, and with a very high flow rate, Kaiser claimed to obtain much better results than had been previously found, viz. a maximum output of 1370–1825 kg. HNO_3 per sq. ft. of catalyst per 24 hours. The actual yield appeared to be about 480 kg., but this has doubtless been improved.

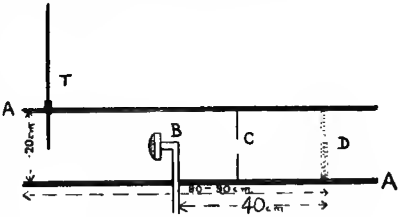

FIG. 59.—Kaiser Ammonia Oxidation Apparatus.

A, tube; B, ammonia supply pipe; C, diaphragm; D, platinum nets; T, thermometer.

MODERN CONVERTERS

In the subsequent improvements of the converter the following details have been found important:—

(1) The use of two or more platinum gauzes, separated by a small interval, the lower one being electrically heated to about 800°.

(2) The use of a regulated amount of preheating of the gases passing to the converter (not pre-cooling, as has been recommended).

(3) A rapid flow of gas through the catalyst.

There is some evidence to show that a suitable converter unit should have a sectional area of 1 sq. ft., although both larger and smaller units have been employed. One sq. ft. of catalyst should produce about 1–1·7 tons HNO_3 (reckoned as 100 per cent.) per 24 hours.

The Supply of Oxides of Nitrogen to Vitriol Chambers.—The use of oxides of nitrogen to supply sulphuric acid chambers instead of nitre has already been successfully introduced in England, and the necessary apparatus has been more or less standardized. In this way a considerable saving of nitre can be brought about, as by no means inconsiderable quantities of oxides of nitrogen have to be supplied to make up losses in the chamber process. The exact amount varies considerably with the type of plant used (cf. p. 34), and also with local practice. The source of the loss is generally believed to be reduction to N_2O, or even N_2 in the chamber process (cf. p. 34), but it is more probable that a large part is due to reduction of HNO_3 and $SO_2(OH)(NO_2)$ to NO by the coke packing generally used in the Gay Lussac towers. In more modern plants this packing is replaced by Lunge-Rohrmann plates, or rings, or other more suitable inert packing. The total quantity of nitre (in the form of oxides of nitrogen) which must be kept circulating in the system for efficient working is much larger than that supplied to make up for losses; hence, in starting a chamber plant a sufficiently large excess of oxides of nitrogen must be introduced. The amount of total circulating nitre has been variously stated from 9–25 per cent. of the sulphur burnt per 24 hours. About 10 parts is apparently the normal working with large chamber space; with very good chambers 9 per cent. is sufficient; with smaller chamber space 15–20 per cent.; and with "intensive" working 25 per cent., of the sulphur burnt may be used.

The extraordinary variations in practice, as to the supply of nitre to make up for loss, are shown in the following table, all the figures in which refer to a single district (Widnes). It is evident that the question of nitre supply is dealt with quite empirically, and there is every reason to believe that usually more nitre is used than is really necessary. About 2 per cent. on the sulphur burnt has been successfully used.

Pyrites burnt per week in tons.	Cu. ft. chamber space per lb. S burnt per 24 hours.	Percentage nitre on S burnt.	Capacity of Gay Lussac in cu. ft. per ton pyrites burnt per week.	Total acidity of waste gases as grains SO_3 per cu. ft.
52	21·0	3·50	—	—
350	18·0	5·00	65·8	0·87
210	17·8	4·70	18·7	2·10
125	28·0	4·00	36·1	0·65
98	17·8	4·20	32·4	2·88
240	21·0	4·25	24·0	1·71
250	28·3	3·75	15·7	2·34
150	21·0	—	37·8	0·79
250	19·3	5·00	20·5	1·90
60	22·3	—	27·5	3·89
260	22·0	3·30	33·7	1·60
117	21·0	4·00	53·5	1·30
183	20·0	—	21·5	2·94
70	17·5	—	79·6	0·70

The Absorption Towers.—When one constituent of a mixture of gases is to be separated by dissolving it in a liquid in which it is more soluble than the remaining constituents, the operation is conducted in the laboratory by means of wash-bottles, or absorption bulbs, in which the gaseous mixture is bubbled through the liquid solvent. Occasionally, when a sparingly soluble gas is to be removed, a vertical tube filled with pieces of pumice or glass beads is used, the liquid being dropped down the tube and the gas passed upwards. This last arrangement has the additional advantages that the process may be made continuous, fresh liquid being continually brought in contact with the gas, and that it operates on the counter-current principle, the fresh solvent being brought in contact with the nearly spent gas passing upwards from the lower part of the tube, and the more or less concentrated solution in the lower part of the tube meeting the richer gas entering there. In this way two results are achieved which are not attainable with the wash-bottle—

(1) The last traces of the soluble gas are removed, since these are taken up by the fresh solvent, in which the rate of solution is rapid—the rate of solution being approximately proportional to the difference between the concentration of the solution used to

dissolve the gaseous solute, and the concentration of the solution saturated under the given partial pressure of the gas (cf. p. 68).

(2) The concentration of the liquid solution is that corresponding with the partial pressure of the solute in the original gaseous mixture, and is therefore the maximum attainable. The velocity of solution is also greater the richer the gas phase is in the soluble constituent.

Two cases may arise when a gas is dissolved in a liquid solvent, in the manner described—

(i) The gas passes into solution, and any chemical interaction between the gas dissolved and the solvent does not give rise to the emission of another, less soluble, gas; *e.g.* the solution of sulphur dioxide, carbon dioxide, and hydrogen chloride in water.

(ii) The chemical interaction between the dissolved gas and the solvent produces another, less soluble, gas, which, at a given concentration, is emitted from the solution; *e.g.* the solution of nitrogen dioxide in water, when nitric oxide is given off—

$$3NO_2 + H_2O = 2HNO_3 + NO$$

On the large scale, the apparatus used for the absorption of gases is a modification of the laboratory column filled with beads, down which a liquid trickles, and is called a *tower*. Examples of such towers have already been met with in the Gay Lussac and Glover towers (the latter, however, having a more complicated function than simple absorption), and the Gossage towers for the absorption of hydrochloric acid.

The absorption tower, when complete, will consist of three parts—

(1) The *tower* itself, consisting of a cylindrical structure, with inlets and outlets for gas at the bottom and top, respectively, and inlets and outlets for liquid at the top and bottom, respectively.

(2) The *packing*, which replaces the glass beads in the laboratory apparatus.

(3) The arrangement for circulating the liquid through the tower (in case saturation is not attained by a single passage) called the *lift*.

The necessity for circulating the liquid is caused by two factors—first, the large volume of liquid which is required to wet the packing in the tower, and is therefore in excess of that required for the volume of gas passing during the descent of the liquid in the tower; and, second, the possibly slow rate of solution of the gas in the liquid. It may be necessary, as is indicated by the two principles of tower design, viz. the removal of as much of the soluble gas as possible, and the necessity of obtaining a concentrated solution, to pass the gas through several towers, the last being fed with pure solvent, the next to the last with the solution from the base of the last tower, and so on. These towers are really equivalent to a very tall single tower, with the last tower forming the top section, and the first tower the bottom section. Another plan is to circulate the liquid in each tower separately, but to add fresh solvent in addition to the top of the last tower. An equivalent bulk of solution is drawn off from the base of this tower and added at the top to the liquid circulating in the next forward tower, the same volume being taken from the base of this tower and passed to the top of the next. The concentrated solution is finally run off at the same rate from the bottom of the first tower. It may happen, on account of temperature differences, that the strongest solution does not issue from the first tower, but from the second tower in the series; for instance, the first tower may act as a cooler, and the cooled gas is then absorbed to the maximum strength in the second tower. The first tower may also be used for purification or to remove dust. The two methods of tower circulation just described may be called the *continuous* and the *progressive* methods respectively. Another method is to withdraw a portion of liquid from the base of each tower, but this is rarely used.

The main features of each part of the tower system may now be considered in more detail (Fig. 60).

(1) *The tower.*—This is built up of suitable materials and dimensions, these being determined by three considerations :—

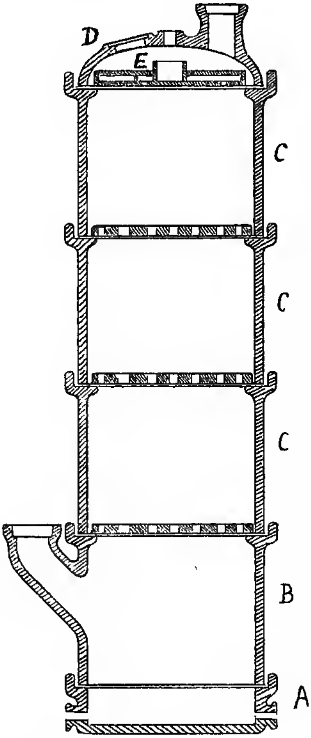

FIG. 60.—Absorption Tower.

A, saucer; B, bottom section; C, C, C, intermediate sections; D, cover; E, distributing plate.

(i) *Mechanical.*—The tower must be sufficiently strongly built to stand the crushing weight of the upper part; it must be as tall as possible to give sufficient contact; it must not be too wide on account of the difficulty of obtaining uniform wetting of the packing, nor too narrow, when the gas would pass through with too high a velocity and would not remain long enough in contact with the liquid; and lastly, it must not allow either liquid or gas to leak out. The materials of which the tower is constructed may be bricks, stoneware pipes, or stone slabs. Acid-resisting metal may also be used, but not much is known of the properties of such material over long periods. If the tower is large, it should be built on foundations of reinforced concrete; if relatively small, on a brickwork pier, covered with pitch if the tower is to be used for the absorption of acids. Tall towers, especially if built of pipes, should have a supporting wooden framework or scaffolding. Very heavy pipe sections should be supported separately. The lowest part of the tower, which consists of a *saucer*, should be made especially strong, as it supports the whole of the upper part of the tower. If the tower is built of bricks, these should be specially shaped so that the joints slope downwards into the tower, and liquid will, therefore, always run back wherever it percolates to the outer wall. Such bricks are made for the purpose. If built of stone slabs, these should be trued up and the joints sealed with putty, composed of china clay and boiled tar if for hydrochloric acid, and one of the special lutes described on p. 148, if for nitric acid, or else sealed with a mixture of asbestos powder and fibre and water glass. The slabs are bound with iron bands clamped with bolts. Stoneware pipes have the junctions luted by letting the spigot of each pipe rest in the socket of the lower one, then packing the space between with asbestos rope, which is then covered with lute. Pipe towers are hardly suitable beyond a diameter of 3½–4 ft. and a height of 20 ft., although larger sizes may be used if the crushing weight is taken off the lower sections by scaffolding supports, and the saucer is embedded in concrete. There is no such limit to the height of brick or stone towers; these may be built up to 12 ft. diameter and 60 ft. high. The diameter is usually about one-fifth of the height. In some cases rectangular towers have been built, but the circular section is much to be preferred on account of the more uniform gas flow.

(ii) *Thermal.*—It is often necessary to maintain the contents of the tower at a given temperature. If heat is given out in the reaction proceeding in the tower, the inflowing gas and water (or other solvent) may have to be cooled; the rest of the heat is dissipated from the surface of the tower by radiation and convection, arriving at the surface by conduction through the walls. All these factors may be controlled by well-known calculations, although this part of tower design has had little attention. Special arrangements may be introduced for lowering the temperature in the tower, as with the Cogswell coolers in the Solvay tower (p. 87).

(iii) *Chemical.*—The materials of the tower must not be attacked by the gas or liquid. Ordinary bricks will hardly ever be suitable, acid-resisting blue bricks from North Wales, or acid-resisting blocks (p. 111), set in silicate mortar composed of ground fireclay, asbestos, and water glass, may be used. If stone is used, it should be granite if for nitric acid, or Yorkshire flag boiled in tar for hydrochloric acid. Another chemical factor is the free space required in the tower if a gas reaction goes on inside. Thus, in the absorption of oxides of nitrogen, nitric oxide is evolved, which has to be reoxidized by the excess of oxygen present, and then reabsorbed, and so on :—

$$3NO_2+H_2O=2HNO_3+NO$$
$$2NO+O_2=2NO_2$$

The second reaction requires time for its completion. In a 10-per-cent. mixture of NO_2 and air (by volume), 2½ minutes' contact in the towers should be allowed, and with 10,000 cu. ft. of gas passing through the towers per hour, the capacity of the towers will have to be at least 350 cu. ft. The *free* space, to which this calculation refers, is the portion of the tower not occupied by packing; the latter may take up from 10 to 80 per cent. of the space inside the tower, according to the type of packing used. With a packing taking up 20 per cent. of the tower space, the capacity of the towers, for the above example, will therefore have to be $350\times100\div80=435$ cu. ft. If the towers are constructed of stoneware pipes 3½ ft. in diameter, a total length of $435\div(1{\cdot}75)^2\times3{\cdot}17=45$ ft. is required. This could be built up of four towers, each 11 ft. in height, as this height can be made up of three lengths of 3-ft. pipe, together with the cover and saucer. A certain amount of space is provided by the connecting pipes between the towers, which may vary from 4 in. diameter for 1-ft. towers to 15 in. diameter for 3½-ft. towers. It is better to leave this extra space as a margin of safety, and design the towers alone to have the required space.

The intermediate sections are of plain pipe, the lowest section has a gas inlet pipe, and the saucer has two outlets for liquid, one being usually fitted with a ground-in stoneware stopcock and the other with a ground plug or the outlet for the Pohle lift. The cover of the tower has an outlet for gas at one side, and an inlet for liquid in the centre. It usually also has a glass window for inspection. Below the cover, resting on the lip of the top section of pipe, is a distributing plate, for spreading the liquid fed into the tower over the packing. This is a stoneware plate with perforations and ribs, as shown in Fig. 61.

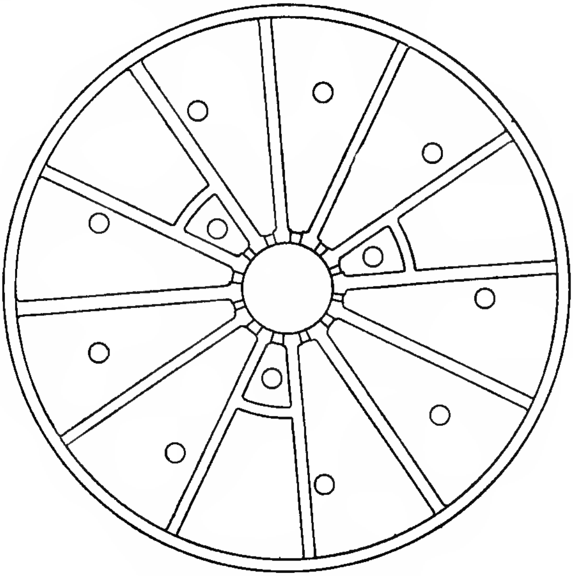

FIG. 61.—Distributing Plate (Plan).

(2) *The Packing.*—This may consist of various materials. If the tower reaction is of the first type, viz. simple absorption, a packing offering the maximum surface is used, such as coke for hydrochloric acid or for the Gay Lussac tower in the chamber process. This should be hard metallurgical coke with no pieces passing through a 3-in. sieve, the larger pieces packed by hand over a grating at the bottom of the tower. For other purposes, blocks of granite, flints, or acid-resisting bricks may be used, or the Lunge-Rohrmann plate packing (p. 28). All these types of packing take up about 80 per cent. of the tower space, and are quite unsuitable for towers in which slow secondary reactions occur,

as in the absorption of oxides of nitrogen. In such cases earthenware cylinders, or "rings" (2 in. diameter and 2 in. high), piled one above the other so as to break up continuous channels, or hollow perforated balls (Guttmann balls), are used. These take up about 50 per cent. and 15 per cent. of the free space, respectively. If Guttmann balls are used, each tower section must be separated by a perforated plate, to carry the weight of the packing, otherwise the packing in the lower part of the tower would be crushed by the weight of that above it. Ball packing is, although probably the best, the most expensive type. Several less expensive patent packings are on the market; some of them are good. The packing should be washed with water before putting into the tower, and the inside of the tower should also be cleaned.

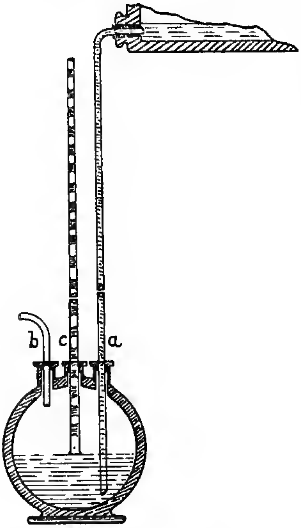

FIG. 62.—Pohle Lift.

a, feed pipe from tower; *b*, pipe for compressed air; *c*, elevator pipe.

The lowest section of the tower, in which is the inlet for gas, is usually left empty; the rest should be filled with packing.

(3) *The Lift.*—This may be on the pressure (Fig. 5) or emulsator (Fig. 6) principle. A very efficient lift on the emulsator principle, which is now largely used, is the Pohle lift (Fig. 62). It consists of a stoneware bottle with three necks. One of these, *a*, serves for the introduction of the liquid to be circulated, say the liquid running from the saucer of the tower. This liquid should run down a tube sufficiently long to prevent its being forced back by the pressure of the compressed air, which is introduced through the neck *b*. Passing through the third neck *c* is the elevator tube, which has a serrated edge below passing halfway

down the inside of the bottle. The liquid runs into the bottle through *a* until its surface touches the serrated edge of the tube *c*, when an emulsion of liquid and air, or, with a slightly less air pressure, a series of short columns of liquid separated by columns of air, is forced up the elevator tube. These lifts work satisfactorily when once the heights of the siphon and elevator tubes, and the air pressure, have been adjusted. The air carried into the towers with the liquid serves for the oxidation of the liberated nitric oxide, and it is quite unnecessary to separate it at the top of the tower by a trap, as is sometimes done. A considerable amount of oxidation occurs in the lifts, as there is an intimate mixing of liquid and air in the elevator tube. The tubes are of glass, about ½ in. diameter, connected by sockets with acid-resisting cement.

Absorption of Oxides of Nitrogen.—The primary products of oxidation of ammonia are, as stated, nitric oxide and steam. These pass out of the converter at about 600°, and are somewhat cooled in passing to the cooling plant through aluminium air-pipes. When the hot gases from the converter cool down, in presence of excess of oxygen, either added in the first place to the mixture passed over the catalyst, or after the catalyst in the form of "secondary air," an oxidation of the nitric oxide to higher, brown, oxides begins. According to Raschig this takes place in two stages :—

(1) A rapid oxidation to the stage N_2O_3.

(2) A slow oxidation to the stage N_2O_4.

Lunge and Berl proved, however, that the oxidation occurred with measurable velocity according to the equation for a termolecular reaction—

$$2NO+O_2=2NO_2$$

Holwech also found that the rate of oxidation of nitric oxide was comparatively slow. According to Norton ("Report") in the case of furnace gases from the arc process, containing 2 per cent. NO in the air, 50 per cent. of this is oxidized to NO_2 in 12 seconds, and 90 per cent. in 100 seconds, at air-temperature.

The results of Lunge and Berl are summarized below. Initial mixture: 125 c.c. NO, 500 c.c. air. Temperature 20° C.

Time in seconds.	Composition of gas expressed as per cent. of original NO.	
	Per cent. NO_2 by volume.	Per cent. NO by volume.
0	0	100
1·76	52·49	47·51
2·64	61·33	38·67
3·96	69·05	30·95
7·92	80·56	19·44
13·78	85·28	14·72
29·92	91·77	8·23
∞	100·00	0

This preliminary oxidation is effected by having the first tower empty, and not circulating any liquid in it. The gases are first cooled to 30° in preliminary air-coolers of acid-resisting metal, and in silica spirals immersed in water, most of the water produced in the oxidation being removed, containing some nitric acid. The tower system therefore consists of a preliminary empty *oxidation tower*, followed by a series of *absorption towers*. Part of the secondary air, required for the conversion of NO into NO_2 is introduced by the Pohle lifts into the absorption towers; the rest is added to the cooled gases passing into the oxidation tower.

By reason of the high velocity of the gas current, and the slow rate of oxidation of NO to NO_2, it is possible by special cooling apparatus to separate up to 75 per cent. of the steam without taking out more than 1 per cent. of the total nitric acid produced, and so to pass on a rich gas mixture to the first absorption tower, which leads to the production of a stronger acid. In addition, the concentration of the oxides of nitrogen is increased by the removal of the steam, and further oxidation therefore takes place more rapidly. The condensed water, together with enough additional water to produce acid of 55 per cent. is added to the top of the last tower. If nitric acid quite free from ammonia is required, only pure water should be added to the last tower, and the condensed water either used for the preparation of ammonium nitrate or thrown away. If only the condensed water is used and no extra water added, an acid of 78 per cent. strength would be produced, but, as described below, it is not possible to attain this strength by direct absorption, as the latter ceases at about 68 per cent. Acid of 60 per cent. may, however, be produced in the towers.

If the gases are brought in contact with water or an alkaline absorbent, the reactions are somewhat complicated. Foerster and Koch with discussion of previous work, state that the following reactions occur :—

$$(1)\ N_2O_4+H_2O=HNO_2+HNO_3$$
$$(2)\ 3HNO_2=HNO_3+2NO+H_2O$$

Therefore the total reaction is—

$$(3)\ 3NO_2+H_2O=2HNO_3+NO$$

If absorption occurs at higher temperatures, say about 50° C., practically no nitrous acid is produced, and reaction (3) occurs directly.

The NO may then be further oxidized by the excess of air to NO_2, and finally the whole of the NO_2 converted into nitric acid. But it is known that even under ordinary conditions traces of N_2O_3 are formed according to the equilibrium—

$$(4)\ NO_2+NO \rightleftarrows N_2O_3$$

and this would be absorbed as nitrous acid—

$$(5)\ N_2O_3+H_2O=2HNO_2$$

Foerster and Koch found that if a mixture of 1 vol. NO+2 vols. O_2 is passed into water, rapid absorption occurs until nitric acid of 40 per cent. is produced. Up to 50 per cent. acid the absorption is slower, and then it rapidly diminishes until a concentration to 68–69 per cent. is reached, beyond which no further absorption occurs. This limit is explained by two circumstances—

(i) The volatilization of HNO_3 which is carried away by the gas current.

(ii) The formation of a hydrate, $HNO_3.2H_2O$, in solution, and the great diminution of concentration of "free" water when the strength of the solution exceeds this.

Helbig observed that if a mixture of NO and ozonized air is led into water, rapid absorption occurs, and HNO_3 is produced. Ozone also oxidizes pure liquid N_2O_4 to crystalline N_2O_5, which gives nitric acid with water. Foerster obtained over 80 per cent. acid by leading NO+ozone into water. Warburg also observed that NO_2+ozonized air is rapidly absorbed by dilute alkali, whereas NO_2 alone is only slowly absorbed (cf. below). Ozone with N_2O_4 or N_2O_5 produces some higher oxide, NO_3 or N_2O_7.

If the gases are absorbed by alkalis, peculiar results are obtained (cf. Leblanc, *Zeitschr. Elektrochem.*, **12**, 541, 1906). If the brown fumes from $2NO+O_2$ are shaken immediately with alkali a mixture of equimolecular proportions of nitrite and nitrate is produced—

$$N_2O_4+2KOH=KNO_3+KNO_2+H_2O$$

This is a slow reaction (cf. Nernst, *ibid.*, p. 544). But if the liquid is allowed to stand in contact with the gas for a time, and then shaken, *nitrite* predominates. This is explained by the production of NO, and formation of N_2O_3, which is rapidly absorbed, by the water in the surface of the liquid—

$$N_2O_3+2KOH=2KNO_2+H_2O \text{ (completely)}$$

Thus we have the reactions—

(1) $2NO+O_2 \rightleftarrows 2NO_2$ (slow)
(2) $NO+NO_2 \rightleftarrows N_2O_3$ (rapid)
(3) $N_2O_4+2KOH=KNO_2+KNO_3+H_2O$ (slow)
(4) $N_2O_3+2KOH=2KNO_2+H_2O$ (rapid)

It is found that the rate of absorption of oxides of nitrogen in *water* is diminished by rise of temperature, Another factor which has not been mentioned above because even less is known about it, is the influence of temperature on rate of solution by altering the relative amounts of NO_2 and N_2O_4 in the gas. It is very probable that the polymerized form of the oxide is dissolved more slowly or more rapidly than the simple form. Above a certain concentration of HNO_3, oxides of nitrogen as such exist in the solution (N_2O_3 or N_2O_4) and the equation—

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

is then no longer sufficient to explain all the reactions. These oxides of nitrogen colour the liquid blue (N_2O_3), green ($N_2O_3 + N_2O_4$), or yellow (N_2O_4), according as it contains more or less water.

It is found impossible in practice to absorb the whole of the oxides of nitrogen in water in the form of nitric acid. When the gases become very dilute, the rate of oxidation of NO to NO_2 is very slow, and the last portions are usually swept out of the towers with the effluent gases. It is common for the effluent gas to contain 10 per cent. of the oxides passed into the tower, when the latter are very dilute gases obtained from arc furnaces, *i.e.* a gas containing 0·2 per cent. of NO escapes. Even with richer gases, a considerable amount of oxides of nitrogen escape, especially should the temperature of the towers be too high. Various ways of dealing with these gases have been proposed. In the case of arc furnace gas, the problem is not so acute, but when an expensive raw material such as ammonia is in question, it is imperative that as much of the oxides of nitrogen as possible should be absorbed. Two proposals are given below: the first is used at the arc works, whilst the second seems to offer advantages to English practice:—

(1) The residual oxides are sent to a tower down which a spray of caustic soda or sodium carbonate solution is falling Sodium nitrite is produced, according to equations (2) and (4) above. The liquid is circulated until it is neutralized by the oxides of nitrogen, and is then evaporated to produce sodium nitrite.

(2) The residual oxides are passed to a Gay Lussac tower and absorbed in concentrated sulphuric acid, as in the chamber process. It might even be possible to pass the exit gases directly to the vitriol chambers, so as to utilize the oxides of nitrogen, although these are in a very dilute state. In any case the working of ammonia oxidation in connection with a chamber plant offers several advantages.

Alternative Methods of Absorption.—The absorption towers previously described are very bulky, and form the most expensive item of the ammonia oxidation plant. Various proposals have been made with a view to dispensing with the towers altogether, but it must be kept in mind that a certain amount of space will always be required for the reaction—

$$2NO+O_2=2NO_2$$

to proceed whilst the converter gases are passing to the absorption system. In addition, the gases are charged with moisture, which would have to be removed if some of the methods were applied, and this removal in presence of oxides of nitrogen would present difficulties. It would be simplest if the proportions of air and ammonia passing to the converter were such as to produce NO, which, after removal of about 80 per cent. of the water by cooling, could then be dried by sulphuric acid and mixed with sufficient air or oxygen to form NO_2. But it has been found that the efficiency of oxidation falls off appreciably when the air is reduced to the stage sufficient for the production of NO alone, the full efficiency not being reached until enough air is added to form N_2O_3.

If a dry mixture of air and oxides of nitrogen is obtained, the following methods have been proposed for the absorption of the oxides :—

(1) Compression to 5 atm. and then cooling by adiabatic expansion, when the nitrogen dioxide liquefies out as N_2O_4. The cooling must be carried to a point much below the point of liquefaction of pure nitrogen dioxide, because

the temperature-lowering must reach a point at which pure liquid N_2O_4 has a vapour pressure equal to the partial pressure of NO_2 in the gas mixture. If the oxidation to NO_2 is not complete, and some NO is left, then N_2O_3 will liquefy along with the N_2O_4, and the condensing temperature is still lower.

(2) Washing out the NO_2 by liquid solvents, which boil above 50° C., and do not solidify above −50°, and are not attacked by NO_2. These are proposed for use in conjunction with cooling, to prevent the apparatus becoming choked by solid N_2O_4, but might be used at ordinary temperatures if the solubility were great enough. Such solvents are pentachlorethane, tetrachlorethane, nitrobenzene, and carbon tetrachloride. The NO_2 can be removed from the solutions by fractionation.

(3) Absorbing the NO_2 in solids, such as the oxides of lead, copper, zinc, and calcium. In the case of the oxides of the heavy metals the absorption occurs somewhat slowly at about 150° C., with formation of a mixture of nitrite and nitrate, from which the oxides of nitrogen are expelled in a concentrated form by heating to about 200° C.—

$$2ZnO+4NO_2=Zn(NO_2)_2+Zn(NO_3)_2$$
$$Zn(NO_2)_2+=ZnO+NO+NO_2$$
$$2Zn(NO_3)_2=2ZnO+4NO_2+O_2$$

The use of lime forms the basis of the process of Schloesing, which was intended for the treatment of gases from the arc furnaces. The quicklime is specially prepared by slaking ordinary lime, preferably obtained from chalk, dehydrating the slaked lime at a temperature not above 500°–600°, and pressing the calcium oxide into briquettes. If these are heated for several hours at 400°–450° in a stream of air containing oxides of nitrogen, basic calcium nitrate, containing only a trace of nitrite, is ultimately produced. The presence of about 1 per cent. of the oxides of manganese, iron, or chromium, acts catalytically and accelerates the reaction. This process is, however, quite unsuitable for use with gas from ammonia oxidation. In the first place the drying of the gases would offer considerable difficulties. Then the nitrate produced is basic and would not be suitable for the preparation of ammonium nitrate or nitric acid without great technical difficulties and loss of materials, whilst the raw product would not command a price sufficient to pay for the ammonia. Lastly, the absorption process is always attended by a considerable loss of nitrogen in the elementary form—as much as 20 per cent. being set free—

$$2CaO+5NO_2=2Ca(NO_3)_2+N$$

This loss of nitrogen also attends the absorption by the other metallic oxides mentioned above, and although this might not be serious in the case of the arc process, where on account of the cheapness of power it is more important to ensure smooth running of the process than economy of material, yet it could not for a moment be tolerated in the ammonia oxidation process where such an expensive raw material as ammonia is used.

In addition to the above processes, which deal with dry gases, there are a few processes which aim at the production of nitric acid from the moist oxides of nitrogen without the use of absorption towers. These depend on the treatment of the gases with steam and air or oxygen, followed by cooling so as to liquefy out nitric acid directly. These processes appear to offer important advantages, and it is probably in this direction that further advances will be made in the near future.

In Brit. Pats. 15948 of 1911, 4345 of 1915, to Meister Lucius and Bruning, a process is described for the preparation of concentrated nitric acid from 60–62 per cent. acid obtained in absorption towers. The dilute acid is enriched with nitrogen dioxide, NO_2, which easily dissolves in the acid, and the nitric acid containing nitrogen dioxide is subjected in a finely divided state to the action of oxygen. In consequence of the increased concentration of the NO_2 the speed of the reaction is increased in the sense of the equation—

$$2NO_2+H_2O \rightarrow HNO_3+HNO_2$$

The unoxidized part of the NO_2 is expelled by the oxygen introduced at the end of the reaction system, and the nitric acid is obtained practically free from nitrous acid. The NO_2 may be introduced either in the liquid or gaseous state. A small excess of oxygen (2–5 per cent. over the theoretical equation $4NO_2+O_2+2H_2O=4HNO_3$) is used.

If nitric acid containing water is intimately mixed with a larger proportion of liquid NO_2 than corresponds with the maximum solubility, and the liquid is left at rest, two distinctly separate layers are rapidly formed. Each of these homogeneous layers consist of nitric acid and NO_2, and one of them—in most cases that of lower specific gravity—contains a more concentrated acid (under favourable conditions nitric acid of about 100 per cent. strength) and the other layer a more dilute acid than that at first used. The NO_2 may be eliminated from the enriched layer by fractionation, and used again.

Thus, if 15 parts by weight of nitric acid of 81 per cent. strength are shaken with 30 parts of liquid nitrogen dioxide and the mixture left at rest, two layers separate, from each of which nitrogen dioxide is separately removed. In the upper layer there remains an acid of 98–99 per cent. strength, and in the lower layer one of 75 per cent. strength.

If a mixture composed of 60 parts of nitric acid of 75 per cent. strength and 450 parts of nitrogen dioxide is treated under a reflux condenser with a strong current of oxygen, two layers make their appearance on standing. If the NO_2 is removed and the two layers mixed, there remains an acid of 95 per cent. strength. The upper layer alone when freed from NO_2 is an acid of nearly 100 per cent. strength, and the lower layer an acid of about 90 per cent. strength.

If NO_2 and oxygen are passed through water or dilute nitric acid for a sufficient time, the same two layers make their appearance on standing.

In the process of the Saltpetersüre Industrie G.M.B.H., Gelsenkirchen (Brit. Pat. 23385 of 1908), a mixture of nitrogen, oxides of nitrogen, and water is cooled by refrigeration to a temperature below zero, when nitric acid separates, the concentration of the acid obtained being higher the greater the degree of refrigeration. Thus, if a mixture of air, nitrogen dioxide, and aqueous vapour, containing 1 per cent. by volume of NO_2 and so much aqueous vapour that the nitric acid vapour remains slightly superheated at 100° C. (*e.g.* 20 grams H_2O per cu. metre) is cooled, the following results are obtained. When the temperature falls to 30° C. a nebulous condensate of acid of 5 per cent. strength is formed. At 20° the proportion of acid in the nebulous condensate is approximately 17 per cent., at 10° approximately 50 per cent., and at slightly below zero the proportion of acid is 60 per cent. If no part of the condensate is removed during the cooling, all the nitrogen dioxide is converted into 60 per cent. acid. By removing the condensate at different stages of the cooling, condensates of different strengths can be separately obtained.

The Concentration of Nitric Acid.—The tower acid, obtained by absorbing the oxides of nitrogen in water in the towers, is usually about 55–60 per cent. strength nitric acid, and contains very little nitrous acid. It may be used directly for the preparation of ammonium nitrate by neutralizing it with ammonia, but if strong nitric acid (80–98 per cent.) is required, this weak acid must be concentrated.

Several processes for the concentration of nitric acid have been proposed, the following being the most important :—

(1) *By fractional distillation.*—The boiling-points of water and pure nitric acid are 100° and 86°. If, however, a mixture of nitric acid and water is distilled, either a more dilute or more concentrated acid passes off as vapour until the composition of the residue is 70 per cent. HNO_3, which then boils off unchanged at a temperature of 121°. In other words, this is the mixture of maximum boiling-point. If a weaker acid than this is distilled, the residue approaches the composition of the mixture of maximum boiling-point, viz. 70 per cent., and no further concentration is then possible. If, however, a stronger acid, say 80 per cent.,

is distilled, a still more concentrated acid comes over till the residue has attained the 70 per cent. composition. The method of concentration by distillation is, therefore, of very limited application.

(2) *By distillation with concentrated sulphuric acid.*—If concentrated sulphuric acid is added to the weak nitric acid, say 70 per cent., then the vapour produced on heating is much richer in nitric acid, and with a large excess of sulphuric acid practically pure nitric acid may be distilled off. This forms the basis of the usual method of concentration, which may be carried out in two ways—

(1) Discontinuously.
(2) Continuously.

In the discontinuous process, the weak nitric acid is mixed with concentrated sulphuric acid in a cast-iron still, similar to a nitric acid still (Fig. 47), and the strong nitric acid distilled off. The sulphuric acid remaining is then re-concentrated, say in a Gaillard tower, and used over again. This method is somewhat costly, on account of the large consumption of fuel in the distillation and in the re-concentration of the sulphuric acid.

In the continuous process, the vapour of the weak nitric acid is passed up a tower filled with acid-resisting packing, down which strong sulphuric acid trickles. Over every horizontal plane in the tower there will be nitric acid vapour of a definite composition, corresponding with the concentration of the sulphuric acid passing downwards through that plane. Lower down in the tower, where sulphuric acid has become diluted, the vapours contain considerable quantities of water along with the nitric acid, but in the upper part of the tower, where concentrated sulphuric acid enters, the vapours are practically pure nitric acid. The diluted sulphuric acid passing from the bottom of the tower is reconcentrated in a Gaillard tower. A combination of fractional distillation of the weak nitric acid in vacuum evaporators, similar to Kestner evaporators (Fig. 27), and then passage of the enriched vapours to a sulphuric acid column, forms the basis of Collet's concentrating apparatus, used in the Norwegian works. It is one of the most efficient modern types of concentrating plant, but has a very high initial cost compared with a discontinuous still.

(3) *By treatment with liquid nitrogen dioxide.*—If an 80 per cent. nitric acid is agitated with liquid N_2O_4, the mixture separates into two layers. Both layers contain considerable amounts of unchanged N_2O_4, but if they are separated, and the N_2O_4 distilled off, the residue from the upper layer is practically 100 per cent. HNO_3; that from the lower layer is 75 per cent. HNO_3.

If an acid weaker than 80 per cent. is taken, the separation into two layers does not occur, but if a considerable excess of liquid nitrogen dioxide is added, and oxygen blown through the mixture, preferably with violent agitation under a reflux condenser, then at a certain point separation into two layers again occurs on standing. After removal of the N_2O_4, the residues of these layers are 100 per cent. HNO_3 and 75 per cent. HNO_3, as before (cf. p. 255).

The oxygen used in these processes could be obtained as a by-product in the fractionation of liquid air in the process of making nitrogen for the Haber ammonia synthesis or the preparation of cyanamide. The oxidation of the ammonia would produce the oxides of nitrogen, which would then be worked up into nitric acid, by means of the oxygen, in some such process as has been described. If the nitric acid were absorbed in the usual tower system, the space occupied by the latter could be considerably curtailed by the use of oxygen instead of air for the secondary oxidation of the NO to NO_2, either in the oxidizing tower or in the Pohle lifts. The weak nitric acid might then be concentrated by means of oxides of nitrogen, obtained by diverting a part of the converter gas to a suitable drying system, and condensing out the NO_2, say by refrigeration.

Cost of Nitric Acid from Ammonia.—Some estimates of the cost of plant, and the conversion costs, for the ammonia-oxidation process have appeared in the literature. These, however, refer to the old Ostwald type of apparatus, and are higher than the costs for modern plant for three reasons—

(1) The large amount of platinum required in the old apparatus, and the expensive nickel tubes.
(2) The small output of the old converters.
(3) The unnecessarily expensive absorption towers used in the old plants.

A summary of these estimates is given below :—

	Per metric ton Nitric Acid (as 100 per cent.).			
	(1)	(2)	(3)	(4)
Capital cost	£10·50	£10·50	£11·96 (£12·3*)	£7·82 (£8·16*)
Conversion cost to 55 per cent. acid	£4·45	£4·91	—	£4·43
Concentration cost, 55–93 per cent.	—	£2·60	—	£3·02
Conversion cost to 93 per cent. acid	—	£7·51	—	£8·22
Conversion cost to 93 per cent. acid per lb. HNO_3 as 100 per cent. acid ..	--	0·816*d.*	—	0·819*d.*

Washburn estimates the cost of conversion at £2·509 to £3·13 per ton HNO_3 as 55 per cent. acid. The old estimates are too high for modern plants for the reasons stated. Thus for a plant producing 10,000 tons HNO_3 per annum, as 55 per cent. acid, the towers alone on the old estimate would cost more than the complete modern plant. The conversion costs as given are also high; the present cost is probably of the order given by Washburn, viz. about £3 per ton, including 10 per cent. amortization. The concentration cost of £3 per ton given in the older estimates is probably somewhat high for a modern installation, but for the present may be taken as correct. With the prices of ammonia from the various sources, given on p. 221, and the conversion and concentration costs just stated, viz. £3 per ton each, one obtains the following table of production costs, for the preparation of one metric ton of nitric acid by a modern ammonia oxidation plant, with a 90 per cent. overall efficiency. (The capital cost for a modern plant, exclusive of the ammonia section, would be about £2·5–£3 per ton HNO_3 in the form of 55 per cent. tower acid, for an annual production of 10,000 tons HNO_3.)

* With concentration plant.

In the case of synthetic sources of ammonia, a power cost of £3·75 per K.W. year has been assumed (cf. p. 216).

Source of ammonia.	Cost of NH_3 per ton in £.	Cost of HNO_3 as 55 per cent. acid in £ per ton.	Cost of HNO_3 as 97 per cent. acid in £ per ton.	Cost of HNO_3 as 97 per cent. acid in pence per lb.
By-product (estimated)	10·0	6·33	9·33	0·998
,,	(50·0)	(19·7)	(22·7)	(2·43)
Discontinuous cyanamide	25·34	11·45	14·45	1·545
Continuous cyanamide	20·25	9·75	12·75	1·364
Haber	15·0	8·0	11·0	1·177
Serpek	8·414	5·80	8·80	0·942

These figures are, of course, more or less tentative, but it is believed that, as they are based on a careful consideration of all the recent sources of information, they approach much nearer the truth than any previously published estimates, all of which referred to plant which must now be regarded as out of date.

The costs in the table may be compared with the cost of production of nitric acid from Chili nitre by the retort process (p. 159). With nitre at the low price of £8 per ton, the cost of 1 ton HNO_3 in the form of 97 per cent. acid is £18·14, and even with nitre at £5 per ton, which seems a somewhat remote possibility, the cost of nitric acid would be £13·8 per ton, which is higher than any figure stated above with the one exception of the acid made with ammonia produced in the discontinuous cyanamide process. Of course the figures for acid made from recovery ammonia at the usual market rates would be very much higher than any of the above, approaching about £23 per ton HNO_3 as 97 per cent. acid with recovery ammonia at £50 per ton. Even this figure, high as it undoubtedly is, does not represent much more than the price of nitric acid made from nitre when the latter commands the price it undoubtedly will continue to do if not checked by competition.

The figures also indicate the possibility of producing sodium nitrate, say by neutralizing the tower acid with Leblanc lyes, or with soda ash, at a price either less, or at least equal to, that of Chili nitre. One may safely say that the latter product is on the way recently taken by natural indigo.

The production of nitric acid from ammonia is therefore a process worthy of the most serious attention as a peace proposition, and as a war measure it is undoubtedly the best way for this country to become independent of overseas supplies of nitrates. Germany has produced a large proportion of the nitric acid for explosives by ammonia oxidation, and has erected the necessary plant during the war. It is more or less certain that this plant is not operating so efficiently as the most modern plant (full knowledge of which has come to hand from the research work carried out in England during the last year) undoubtedly would.

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SECTION X.—UTILIZATION AND ECONOMY OF SULPHURIC ACID

Utilization of Sulphuric Acid.—There is scarcely a manufactured product known in the preparation of which, either of the raw materials or in the actual process of making the article, sulphuric acid does not play a part. Sulphuric acid may enter into the reactions in four ways—

(1) As an acid, *i.e.* in virtue of its replaceable hydrogen ions.
(2) As a dehydrating agent.
(3) In the preparation of sulphonic acids with organic compounds.
(4) As an oxidizing agent.

(1) As an acid, sulphuric acid is used in the preparation of other acids or of salts. Acids prepared by means of sulphuric acid according to the general schemes—

$$\text{(i)}\quad MX + H_2SO_4 \rightleftarrows MHSO_4 + HX$$
$$\text{(ii)}\quad MHSO_4 + MX \rightleftarrows M_2SO_4 + HX$$

are hydrochloric, nitric, phosphoric, tartaric, acetic, citric, oxalic, stearic, palmitic, and oleic acids, and sulphur and carbon dioxides. Simultaneously with the production of these acids, the salts $MHSO_4$ and M_2SO_4 are formed. Since the sodium or calcium salts of the acids are generally taken, the sulphates of sodium or calcium remain. Sodium sulphate and hydrochloric acid are, for example, simultaneously produced in the Saltcake process. Calcium sulphate is usually thrown away.

Intermediate between these cases is the preparation of soluble "superphosphate of lime" from insoluble calcium phosphate—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2$$

The preparation of phosphoric acid from calcium phosphate, and its subsequent reduction by carbon, is the basis of the older method of manufacturing phosphorus.

The decomposition of the lime soaps of the fatty acids, stearic, palmitic, and oleic, obtained by the saponification of fats with lime (when glycerine is set free), is the process used in the manufacture of candles.

Other sulphates, such as potassium, ammonium, iron, copper, barium and aluminium sulphates, and alum, are prepared for special purposes. The preparation of ammonium sulphate calls for a large proportion of the acid manufactured.

The separation of copper and silver, and of silver and gold, by treatment of alloys with dilute and concentrated sulphuric acids, respectively, is utilized in metallurgy.

Another utilization of the replaceable hydrogen in sulphuric acid is the preparation of hydrogen, by treating iron turnings with dilute sulphuric acid—

$$Fe+H_2SO_4=FeSO_4+H_2$$

This method was formerly used in the preparation of hydrogen for balloons.

Sulphuric acid is also used for cleaning the surface of iron sheets preparatory to tinning; the oxide is removed and the clean surface becomes coated evenly with tin when dipped in a bath of the molten metal.

A peculiar property of the hydrogen ion, which is formed when sulphuric acid, like all other acids, is dissolved in water—

$$H_2SO_4 \rightleftarrows H^{\cdot}+HSO_4{}'$$
$$HSO_4{}' \rightleftarrows H^{\cdot}+SO_4{}''$$

is its powerful *catalytic* activity. Thus, if starch is boiled for some time with very dilute sulphuric acid, it takes up the elements of water, and is converted into invert sugar—

$$C_6H_{10}O_5+H_2O=C_6H_{12}O_6$$

The sulphuric acid remains unchanged. A considerable amount of glucose is manufactured from starch in this way, and is used in making jams, in brewing, etc. It is very essential that sulphuric acid used in the preparation of foodstuffs should be free from arsenic; acid made from sulphur ("brimstone acid") is usually preferred on this account, although ordinary acid from pyrites can be freed from arsenic by the methods already described. A serious outbreak of arsenical poisoning by beer in 1900 was traced to the glucose used in the fermentation, which had been made with arsenical sulphuric acid. Some specimens of the acid used then for the manufacture of glucose deposited crystals of arsenious oxide, As_2O_3, in the carboys. No sulphuric acid which has not been shown by analysis to be free from arsenic should be used in the preparation of foods.

Another catalytic action of sulphuric acid is utilized in the manufacture of ether, although this reaction belongs also to the dehydrating actions of sulphuric acid (see section (2)). A mixture of sulphuric acid and alcohol is heated to 140° C., and alcohol run in continuously. A mixture of the vapours of ether, water, and some alcohol distils off, the sulphuric acid acting catalytically—

$$\text{(i)} \quad C_2H_5OH + H_2SO_4 = C_2H_5HSO_4 + H_2O$$
$$\text{(ii)} \quad C_2H_5OH + C_2H_5HSO_4 = (C_2H_5)_2O + H_2SO_4$$

The two steps in this "catalytic action" can be separately realized and the "intermediate compound" ($C_2H_5HSO_4$) isolated.

If cellulose, in the form of paper, is treated with sulphuric acid containing a little water, it is converted into a parchment-like material, called "parchment paper," which is used for covering the tops of jam-jars, and for wrapping butter and other moist or greasy materials.

Connected with the hydrogen ion, produced when sulphuric acid is dissolved in water, is the use of dilute sulphuric acid in voltaic cells, especially accumulators, for the generation of electric currents. In the case of the accumulator, only the purest acid (from sulphur), especially free from iron, is used, and its density is controlled by a hydrometer. The hydrogen ion in the cells acts as a carrier of the positive current, or, if we assume that only negative electricity exists in the free state as electrons, the hydrogen ion on receiving an electron, is converted into the hydrogen atom—

$$H^{\cdot}+\ominus=H$$

The reaction in the accumulator also involves the change of concentration of the sulphuric acid (see Partington, "Thermodynamics," p. 468).

(2) Sulphuric acid finds considerable application as a *dehydrating agent.* Concentrated sulphuric acid readily absorbs moisture from the air or other gases, and is used for drying gases, such as chlorine which is to be converted into bleaching-powder, or the air which is used for burning pyrites in the Mannheim contact process for manufacturing SO_3. When used for this purpose, the sulphuric acid is usually spread over pumice or coke in a tower. When mixed with water, sulphuric acid gives out a considerable quantity of heat; according to Thomsen, when 1 gram-molecule of sulphuric acid (98 grams) is mixed with *m* gram-molecules of water, the following equation represents the number of gram-calories evolved :—

$$Q=\frac{17860m}{1{\cdot}798+m}$$

The definite hydrates: $SO_3 2H_2O$, $SO_3.H_2O$, $2SO_3.H_2O$, have been isolated in the pure state.

Not only does concentrated sulphuric acid absorb water with avidity, but it is also capable of decomposing many organic compounds containing hydrogen and oxygen, from which it removes the elements of water and leaves a product rich in carbon—in many cases carbon itself. Thus, by the action of concentrated sulphuric acid on sugar, or other carbohydrates, a black mass of finely divided carbon is produced—

$$C_6H_{12}O_6=6C+6H_2O$$

This reaction is utilized in the manufacture of blacking—a mixture of treacle and concentrated sulphuric acid furnishes finely divided carbon; oil is then added.

This destructive action is rather specific, and oils, for instance rape-oil, may be refined by shaking with strong sulphuric acid, when the mucilaginous constituents are charred and separated, and the oil is thus clarified. Hydrocarbon oils such as petroleum, are refined in the same way, and considerable amounts of sulphuric acid are used in petroleum refining.

The dehydrating action of sulphuric acid on alcohol has already been mentioned in connection with ether. In this case, the catalytic activity of the acid is also important. In the preparation of esters from mixtures of alcohols and organic acids, such as ethyl acetate or amyl acetate—

$$C_2H_5OH + CH_3COOH \rightleftarrows CH_3COOC_2H_5 + H_2O$$

the reaction is carried out in the presence of sulphuric acid, which serves the double purpose of removing the water produced (which would tend to stop the reaction by its mass, leading to equilibrium), and also accelerating the reaction catalytically.

Important esterification reactions are the preparation of the ester of glycerine and nitric acid—" Nitroglycerine," as it is incorrectly called, or glyceryl trinitrate, and of the nitro-celluloses, used for collodion, or gun cotton, which are made by treating glycerine, or cellulose, respectively, with a mixture of nitric and sulphuric acids.

A most important series of reactions in which sulphuric acid acts as a dehydrating agent is found in the so-called *nitration* of organic compounds. In this reaction, which occurs when aromatic hydrocarbons or their derivatives are treated with a mixture of nitric and sulphuric acids, a hydrogen atom is replaced by the nitro- group. Thus, with benzene, nitrobenzene is produced, which by reduction gives aniline, $C_6H_5NH_2$.

Toluene gives, as a final stage, trinitroluene, used as an explosive, under the name of " T.N.T."

Phenol on nitration gives trinitrophenol, or picric acid, $C_6H_2(OH)(NO_2)_3$, also largely used as an explosive under the name of lyddite, or melinite.

Various other organic nitro-compounds are used, either as dyes or explosives.

(3) Sulphuric acid acts on aromatic hydrocarbons, or some of their derivatives, in such a way that an atom of hydrogen is replaced by the group SO_3H, with production of a *sulphonic acid*. Thus, benzene, when heated with concentrated sulphuric acid is converted into benzenesulphonic acid—

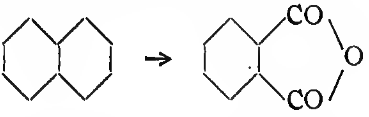
$$C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O$$

If this is converted into the sodium salt, and the sodium benzene-sulphonate fused with caustic soda, sodium phenate is produced, which when treated with acids (even CO_2), forms *phenol*—

$$C_6H_5SO_3Na + 2NaOH = C_6H_5ONa + Na_2SO_3 + H_2O$$

Other sulphonic acids are used in the preparation of dyes.

(4) Sulphuric acid under certain conditions may function as an *oxidizing agent*. Thus, when naphthalene is heated with fuming sulphuric acid, in the presence of mercury as a catalyst, it is oxidized to phthalic anhydride, which is the starting-point in a method for the synthesis of indigo—



Indigo itself is soluble in concentrated sulphuric acid, with the production of a deep blue compound, indigo-sulphuric acid, which is soluble in water.

It is evident from the foregoing summary to what a multitude of uses sulphuric acid may be applied. There are in addition a number of minor uses, but the bulk of the acid of commerce is absorbed in the main industries just outlined, of course in different proportions. The superphosphate industry takes about 35 per cent. of the total acid produced in Great Britain and Germany in normal conditions (and 70 per cent. in America). Rather more than this is used in the manufacture of ammonium sulphate.

Next in importance are the nitration processes, and the production of nitroglycerine, guncotton, and explosives; the salt-cake process; cleaning iron sheet for tinning, and making alum and sulphates; the manufacture of nitric acid; and the refining of petroleum. The other uses, the preparation of ether, phosphorus, sulphonic acids and dyes, for accumulators, glucose, etc., come next in importance.

ECONOMY OF SULPHURIC ACID.

In a state of war, the uses of sulphuric acid must be restricted as far as possible to those immediately concerned with the manufacture of munitions, viz. explosives, such as nitro-glycerine, guncotton, picric acid, T.N.T., etc. For this purpose, not only is sulphuric acid required as such, in the nitration processes, and the preparation of phenol (which also requires caustic soda), but also in the preparation of nitric acid, where the latter is made (as it is at present exclusively in this country) from nitre by the retort process. A state of war, therefore, requires a strict economy in the use of sulphuric acid. This implies restriction in all non-essential uses, and economy in—

(1) The use of sulphuric acid in the preparation of nitric acid. By the oxidation process (Section IX) nitric acid can be made from ammonia without the use of sulphuric acid at all.

(2) The use of sulphuric acid in nitration ("Mixed acid").

It has already been mentioned that the imports of pyrites put a heavy demand on shipping, and attempts have been made to revive the use of British pyrites (see p. 18). Germany has probably also felt the shortage of pyrites. The roasting of zinc, copper, and lead ores could supply a considerable amount of sulphur dioxide, and it is even possible that some sulphuric acid in Germany has been made from gypsum (p. 48; *Chem. Trade Journ.*, Nov. 27, 1915), although there should have been a sufficient supply of sulphide ores to overcome the curtailed supply of pyrites.

A considerable economy of sulphuric acid has been effected by the utilization of nitre-cake, or acid sodium sulphate, $NaHSO_4$, for various processes requiring sulphuric acid. An account of these uses has been given on p. 160.

SECTION XI.—THE POTASH INDUSTRY

Potassium Salts.—It has been stated in connection with the history of the Soda Industry that the use of potassium salts, such as the carbonate and caustic potash, was largely superseded by the utilization of the corresponding sodium compounds when the latter could be prepared from common salt by the Leblanc process. There are a large number of cases in which the two elements are interchangeable. This indifference occurs when it is only the negative radical of the salt which is the important constituent, as is the case, for instance, when an alkali is required, and the hydroxyl ion is just as effective when paired off with the potassium ion as with the sodium ion; or the oxidizing effect of the chlorate ion, which is manifested equally whether it is present as sodium or as potassium chlorate. Even in the latter case it has been found that the sodium salt is usually preferable on account of its greater solubility, and the possibility this gives of obtaining the chlorate ion in greater concentrations and hence more powerful oxidizing capacity. But this is only quite a secondary consideration, and if rubidium chlorate, for instance, were found to be more soluble than potassium chlorate, and if rubidium were a common element, then rubidium chlorate could be just as usefully substituted for potassium chlorate as is the sodium salt in actual practice. In the laboratory it is usually a matter of indifference whether a solution of potassium or sodium hydroxide is used, because the active substance is generally the hydroxyl ion common to both, and on a large scale even lime is often used as an alkaline reagent, *i.e.* as a source of hydroxyl ions, although its smaller solubility and the insolubility of the salts produced in many cases must be set off against its cheapness.

When it is the cation, or metallic radical, which is the active agent, all these considerations are no longer valid and the salts of potassium and sodium are no longer interchangeable. One of the most important of these cases is that of plant nutrition. It has been shown by direct experiment that, under otherwise identical conditions, plants can grow in solutions or soils quite free from sodium salts, but are unable to develop in the absence of salts of potassium (Hellriegel and Wilfarth). The soil has the property of retaining potassium salts by absorption and chemical interaction (Way, 1850), whereas sodium salts percolate through. An equivalent of the calcium ion is set free when the potassium ion is retained. The absorptive power is greatest in soils rich in humus and clay, and appears to be effected chiefly by interaction with the complex zeolite silicates, the calcium, magnesium, and sodium bases in the latter being exchanged for potassium. Some insoluble potassium humate is also precipitated, and calcium sulphate or chloride passes into solution. In this way the very small amounts of potassium compounds in the water of rivers, lakes, and seas, in which sodium compounds are invariably present in relatively large amounts, becomes clear. As successive crops are taken off the soil, the potassium salts in the latter are impoverished, and a time comes when the soil is rendered so poor in potash that it becomes useless for purposes of agriculture. Dyer in 1894 concluded that this limit is reached when the soluble potash in the soil, *i.e.* soluble in a one per cent. solution of citric acid and therefore likely to be assimilable by plants, falls below 0·01 per cent. Smetham estimates the mean available potash contents of the soils of the United Kingdom as 0·015 per cent., and concludes that most of these soils contain a reserve of potash large enough to enable their cultivation to be carried on in spite of the stoppage of the supplies of potash from Stassfurt, until other sources become available. In 1900 no less than 3,000,000 tons of potash salts were produced at Stassfurt, of which 1,158,000 tons were used for agricultural purposes in various countries. In 1913 potash salts equivalent to 1,110,000 tons K_2O were produced, of which half were exported, 32,000 tons K_2O coming to the United Kingdom. The cultivation of the sugar beet in particular requires much potash.

Since we have seen that plants require potassium salts for their growth, and derive these from the soil, serving in their turn as the food of animals, it is clear that there must be a distribution of potassium throughout the three kingdoms of Nature, and in some cases its amount will have accumulated to such an extent as to form a source from which supplies of the element can profitably be obtained.

The chief natural sources of potassium salts are :—

1. *The Sea.*—Sea water contains on an average 0·5 to 0·7 gram of potassium per litre.

COMPOSITION OF SEA WATER ACCORDING TO REGNAULT.

Total solids	3·53 per cent.	
Composition of solids :		
Sodium chloride ..	76·49	
Potassium chloride ..	1·98	(equal to 0·5 gram K per litre)
Magnesium chloride ..	10·20	
Magnesium bromide ..	0·06	
Magnesium sulphate ..	6·52	
Calcium sulphate ..	3·97	
Calcium bicarbonate ..	0·08	
	99·39	

These potassium salts are recovered from sea water in two ways :—

(i) As a by-product from the manufacture of "solar salt" (cf. Section I). 1 cubic metre of sea water yields about 64 litres of mother liquor after separation of the common salt, which is worked up as described under "Salt," and yields potassium in the form of carnallite, $KCl.MgCl_2.6H_2O$, from which KCl could be recovered as described under the Stassfurt Industry. For every ton of common salt separated there would be about 75 lbs. KCl in the mother-liquors. Under the severe competition of Stassfurt the economic recovery of this by no means inconsiderable quantity of potash was financially impossible, but newer conditions may alter the case in countries where much solar salt is produced, and where no other sources of potash exist; in Italy, for instance, these *salinas* or mother liquors are estimated to supply all the potassium required.

(ii) Sea plants ("seaweeds") absorb potassium salts from the sea water, and when they are burned this is left in the ash. The ash of seaweeds, called *kelp*, was once in fact a very important source of potassium salts, and may again become so, as will be explained later on.

2. *Minerals.*—The crust of the earth contains 2·4 per cent. K_2O as silicates in the form of primitive rocks, *e.g.*—

Orthoclase, or potash felspar: $Al_2O_3.K_2O.6SiO_2$.
Muscovite, or potash mica: $3Al_2O_3.K_2O.4SiO_2$.
Leucite: $Al_2O_3.K_2O.4SiO_2$.
Apophyllite (and other zeolites), $4(CaO.2SiO_2.H_2O).KF$.

By "weathering," *i.e.* by the combined action of water and carbon dioxide or carbonic acid, especially when assisted by the pulverizing action of frost in causing occluded water to solidify and break up the rock by its expansion, these silicates are slowly decomposed and give up soluble potash, which is retained by the soil and passes into plants. It has not yet been found possible economically to extract potash from such rocks, although attempts have repeatedly been made. Other mineral sources are the deposits of nitre, KNO_3, in India, which we have already referred to as a source of nitric acid (p. 137) and which has been utilized during the war; potassium sulphate in "alum rock," or *alaunite*, $3Al_2SO_6.K_2SO_4.9H_2O$, which is formed in trachyte, or other rocks which have been subjected to the action of volcanic sulphur dioxide. The most important deposits of potassium salts are, however, those in Stassfurt, in Alsace, and in the north of Spain.

3. *Vegetable and Animal Sources.*—Wood and plant ashes; vinasse cinder; suint.

The Kelp Industry and Iodine.—At first the kelp-burning industry, carried out for centuries on the coasts of Scotland, Ireland, Normandy, and Spain, was chiefly directed to the preparation of alkalies. With the discovery of the Leblanc process this demand declined, and the kelp industry has only been maintained by the recovery of iodine, which also occurs in most seaweeds (not, however, in *salsola*, from which *barilla* was prepared). The iodine industry was started early in the nineteenth century in Glasgow, by Dr. Ure, and is now of considerable importance there, although only three works are in operation. Recently nine or ten works have been established in Norway, and several are scattered throughout Japan. The Canadian Potash and Algin Co., Sydney, British Columbia, proposes to extract potash and iodine from seaweed on the Pacific coasts. In Scotland only *drift-weeds* are used; especially the *Laminaria digitata* and *L. stenophylla*—the "red wracks," which are entirely submerged by the tide, but are torn up by storms and cast ashore. Only these two (which contain about half a per cent. of iodine) are worth burning. In Japan other kinds are used in addition, and this country is now able to export large quantities of iodine, besides producing potash salts for home consumption. In kelp-burning the weeds are burnt in pits, and should yield a loose ash containing 23–30 lbs. of iodine per ton; actually 12 lbs. is the average, since the calcination, carried on by crofters and small farmers, may be done at too high a temperature, producing a fused slag, or else the iodides are allowed to be washed out of the weed by rain. The kelp is lixiviated in rectangular iron vats with a perforated bottom, heated by steam. The solution is evaporated in iron pans and the salts fished out; these are called *plate sulphate*, and consist of impure potassium sulphate. On cooling the liquor concentrated to 62° Tw. potassium chloride separates of 90 per cent. purity. Formerly 2500–3000 tons of this salt were produced per annum, but the production was practically given up owing to the competition of Stassfurt, and the crude potassium salts are used as fertilizers. On further evaporation crude sodium chloride, called *kelp salt*, separates. The mother-liquor contains the iodine as potassium iodide. It is mixed with sulphuric acid, allowed to settle, and strained off into the stills, consisting of iron pots with dome-shaped lead covers communicating with trains of earthenware receivers called *udells*. Manganese dioxide is added and the iodine distilled off. The iodine is purified by resublimation in porcelain pans. If more manganese dioxide is added, bromine is evolved, but usually the residual liquor is thrown away. This old process is exclusively used in this country, the processes of Stanford (1863), established in the Outer Hebrides, being no longer worked. In the Char process of Stanford the sun-dried weed was charred slowly in iron retorts at a low temperature, when acetic acid, tar, and ammonia, were to be recovered. In practice only an evil-smelling tarry water was obtained. In the Wet process, the weed was boiled with a solution of sodium carbonate and filtered. Fairly pure cellulose, amounting to 15 per cent. of the weed and called *algulose*, was left, which it was suggested could be used for making paper, and on acidifying the filtrate with sulphuric acid a peculiar colloidal substance called *algin* was precipitated, which was to be used for making jellies, sizing fabrics, and as a glue. The filtrate containing the iodides was evaporated down and neutralized with limestone, filtered, and the filtrate distilled with sulphuric acid and manganese dioxide. Stanford's processes are no longer used, apparently owing to the difficulty of obtaining a regular supply of weeds under the present system of collection, the failure of the tar in the char process, and the insufficient demand for algin products.

In France the liquors from kelp are worked up differently. They are treated with hydrochloric acid and saturated with chlorine. The iodine is precipitated, and is filtered off, washed, and resublimed in earthenware retorts and receivers. If the residual liquor is evaporated down and distilled with manganese dioxide and sulphuric acid, bromine is obtained. The process has fallen off in recent years owing to competition from the Chilian and Stassfurt sources. In Russia, iodine is now being made to some extent from the Black Sea algæ at Ekaterinoslav. In the caliche or crude sodium nitrate deposits of Chili iodine occurs in the form of sodium iodate, $NaIO_3$, to the extent of 0·01–0·15 per cent. The mother liquor contains about 22 per cent. of $NaIO_3$, and is run into lead-lined vats, where it is treated with dilute sulphuric acid and a solution of sodium bisulphite, $NaHSO_3$—

$$I_2O_5+5SO_2=I_2+5SO_3$$

The liberated iodine at first reacts with the excess of sulphurous acid, and only when this is used up does the iodine appear—

$$I_2+H_2O+H_2SO_3=2HI+H_2SO_4$$
$$HIO_3+5HI=3H_2O+3I_2$$

The iodine is formed as a precipitate which, if filtered off, washed, and pressed into blocks, contains 80 per cent. iodine.

The problem of obtaining potash salts from seaweed has again come to the front, especially in America, where difficulties with the Stassfurt monopoly arose in 1910. The seaweeds of the Pacific coast contain about 3 per cent. K_2O on the dry weed, and are therefore richer than the Scotch weeds, although the latter contain more iodine. It was proposed to collect the weed by dredgers and burn it scientifically after drying by steam, but the process does not appear yet to be used on a large scale, although much work has been done by the United States Government on the subject.

Wood and Plant Ashes.—Wood ashes may contain from 2·5 to 12 per cent. K_2O together with lime, magnesia, and phosphoric acid. Potash salts predominate in the twigs and leaves; the solid wood contains much less. If much silica is present, as in straw, sugar-cane, and grasses, the ash contains chiefly potassium silicate, which is not utilizable, but the chief product otherwise is potassium carbonate. The manufacture of potassium carbonate from this source is carried on chiefly in Russia, where there were eleven factories in 1906 (the factories in the Caucasus produced 100,000 tons of 90 per cent. K_2CO_3 annually from sunflower stems), in Transylvania, Illyria, Canada, and the United States. The average annual production of wood per acre in temperate climates is 1·1 tons, of which 1 per cent. is ash containing 5 per cent. K_2O. This amounts to a yearly production of only 1·25 lbs. K_2O per acre. Since the discovery of the Stassfurt deposits the industry has declined; at present the potash derived from wood (excluding plants) does not amount to more than 10,000–15,000 tons per annum. In 1873 about 20,000 tons were produced. The process adopted is very primitive: the wood is burnt in large pits, the ashes sprinkled with water, worked up, and lixiviated in casks with false bottoms, the liquor being run off at a density of 32° Tw. and boiled in large cast-iron cauldrons to dryness. The residue is heated to redness, and forms *potashes*. This is sorted, and a part is refined by redissolving, evaporating and calcining, and forms *pearlashes*, used in the manufacture of flint glass after a further refining by calcining with sawdust, lixiviating and recalcining. Other vegetable sources are cottonseed-hull ash (10–40 per cent. K_2O, formerly used for tobacco-crop top-dressing in the Connecticut Valley), weeds such as wormwood, marigold and tansy, and the ashes of Indian corn cobs (50 per cent. K_2O), and tobacco stems (6 per cent. K_2O). A commission in Italy is investigating the extraction of potash from the press-cake from olive oil making.

Vinasse or Schlempe (Beet-sugar Molasses).—Dubrunfaut in 1830 pointed out that beet-sugar molasses, which is unsuitable for food, is rich in potash. The manufacture of potash from this source was however not begun till 1850 in France, Belgium, and Germany. The process is still used in France, and in Germany 15,000 tons of KCl were made in this way in 1883, but lately the German practice has been to extract the sugar from the molasses by the osmose or strontia processes, and the potash in the mother liquors is put back directly to the soil. In the French process, the molasses, called *vinasse* (*schlempe* in Germany), is neutralized with lime and evaporated in a special type of furnace called a Porion furnace, in which it is splashed in the fire gases by revolving paddles until it becomes thick. The syrup is then put on the hearth of a reverberatory furnace, where it is allowed to catch fire and burn to a coke, called vinasse cinder, containing 30–35 per cent. K_2CO_3, 18–20 per cent. Na_2CO_3, 18–22 per cent. KCl, etc. This is lixiviated. A preliminary evaporation in triple-effect vacuum pans has been used since 1896.

In the Vincent process, used only at Courrières, the vinasse is distilled in an iron retort, when trimethylamine and methyl chloride are obtained. By passing trimethylamine through a red-hot tube, hydrocyanic acid is produced, which is absorbed in soda to produce sodium cyanide (Dessau process).

In the Effront process, formerly used at Nesles on the Somme, the vinasse was fermented, when acetone, alcohol, ammonium salts and other products were obtained.

Suint.—Suint is an animal source of potash, being a potassium soap of sudoric acid present in raw wool. From wool washings about 150 tons of potash per annum are extracted by the firm of Maumené and Rogelet at Rheims and Roubaix, the brown liquor being evaporated and calcined. The wool imported into the United Kingdom annually would yield 300 tons of potash, all of which is lost in streams; 100 parts of raw wool yield 5 parts of potassium carbonate.

Mineral Sources.—The richest mineral sources of potassium salts are—

(1) The Stassfurt Deposits (1839).
(2) The Alsatian Deposits (1904).
(3) The Spanish Deposits (1915).
(4) Felspar.

The Stassfurt Deposits.—There have been salt works at Stassfurt for a long period; formerly they belonged to the Duke of Anhalt, but were sold to the Prussian "Fiskus" in 1796. In 1830–40 common salt was found by boring south of the Harz mountains, in the Thuringian basin, and rich brines discovered, with which the weaker Stassfurt brines could not compete, the latter works closing down in 1860. On April 3, 1839, a boring was begun at Stassfurt, and in 1843 at a depth of 265 metres the upper covering of salts was reached, and the boring was continued for 325 metres without reaching the bottom. The brine was bitter, and contained KCl and $MgCl_2$. Dr. Karsten and Prof. Marchand concluded, however, that pure salt would be found at greater depths, and in 1852 the sinking of two shafts was begun. After five years' perseverance, pure salt was struck in immense quantities at a depth of 330 metres, in reaching which a depth of 250–280 metres of potassium salts was penetrated. Similar deposits were found at New Stassfurt, Loderburg, and Douglashall, and a great number of borings made. The ultimate success of this enterprise, carried on through years of disappointment, is one of the triumphs of geological science, and offers a salutary lesson to the business man. The Stassfurt Potash industry is now a German Government monopoly.

Mode of Distribution of Stassfurt Deposits.—These deposits are not confined to any particular geological formation, but occur from the Permian to the Tertiary, although the Stassfurt deposits underlie the "Bunter" sandstone of the Triassic period. The arrangement of the deposits is as follows :—

Top.

	Alluvial and Diluvial deposits.
(600–800 ft. thick)	"Bunter" sandstone—Triassic.
	Gypsum, anhydrite, red clay, etc.
	Newer common salt (later formation, often lacking).
	Anhydrite ($CaSO_4$).
	"Salzthon" (three layers, bottom : $CaSO_4$; middle : $MgO+Al_2O_3$; top : clay containing 40 per cent. $MgCO_3$), protecting lower deposits.
(50–130 ft. thick)	Carnallite region.
	Kieserite region—"Abraum" salts (*i.e. above* common salt).
	Polyhalite region.
(2000 ft.)	Older Common Salt.
	Anhydrite.
	Bituminous Sandstone.

Bottom.

These deposits form part of an enormous salt basin in the North German plain, which has been tapped in other places (*e.g.* at Sperenberg, near Berlin). They were probably not deposited by the normal evaporation of sea-water, because of their great thickness, but by the evaporation of an inland lake between ranges of mountains and connected with the sea by a bar, over which autumn gales carried sea-water in quantities insufficient to replace the evaporation. Gypsum was first deposited, but was converted into anhydrite by the action of the concentrated brine (Hoppe-Seyler, 1886), then salt, followed by mixtures of NaCl and Epsom salt, $MgSO_4.7H_2O$, forming the polyhalite region, and finally carnallite. A geological upheaval then occurred, covering up and protecting the deposits with a layer of mud, and allowing the mother-liquors to run off. From a consideration of the thin layers of anhydrite in the salt beds of Stassfurt, supposed to represent yearly deposits of gypsum, Precht (1889) estimated the period of formation at 10,000–13,000 years.

It is significant that extensive deposits of potassium salts have, almost without exception, been discovered sooner or later in the vicinity of deposits of common salt. This is easily understood when the origin of these salts, viz. the evaporation of sea-water, is kept in mind. Thus, the salt deposits of Stassfurt and of Spain are accompanied by carnallite. Is there a similar accumulation of potash lying beneath the Cheshire salt beds, or somewhere in their vicinity, which only awaits discovery to solve the urgent problem of potash supplies? It is at least certain that the geological conditions of Stassfurt and of Cheshire exhibit many analogies, and the question is one which seems worthy of attention.

The Stassfurt Potash Industry.—The raw material is crude *carnallite*, $KCl.MgCl_2.6H_2O$ (the *kainite*, $K_2SO_4.MgSO_4.6H_2O$, is not much worked). This, when treated with water, breaks down to a paste of finely divided KCl and a mother-liquor containing $MgCl_2$ with but little KCl. On heating, the KCl dissolves, and is redeposited on cooling in larger crystals, which are pure as long as the ratio $MgCl_2/KCl$ does not exceed 3. In practice the crushed carnallite is treated with waste liquors; on cooling 80 per cent. of the KCl is deposited. The mother-liquor on evaporation and cooling then yields a crop of carnallite, which is treated again. To avoid dissolving other salts (*e.g.* NaCl, $MgSO_4.H_2O$), the first treatment is carried out as rapidly as possible in dissolvers of cast iron, each provided with a conical bottom in which is a conical gauze sieve, through which steam is admitted. The capacity of a dissolver is 350 cu. ft., 50 tons of mineral being worked up in 24 hours. The liquor is clarified by settling, and adding a little lime, and is drawn off by a siphon. The residue is leached and is then used for filling up old workings to prevent subsidence. The solution is run into wrought-iron crystallizing tanks, 7 ft. by 8 ft. by 4 ft.; after cooling slowly—two to three days—the mother-liquor, which contains one-fifth of the KCl, is separated from the KCl crystals by drawing it off through a plug. The crystals are washed with cold, or in winter tepid, water and centrifuged. The mother-liquor is further evaporated in boilers, then in vacuum pans, or in pans heated by a central flue. The KCl is heated in an iron drum with revolving arms carrying ploughshares, crushing rollers, and discharging scrapers, or else in Thelen pans. Crust formation cannot be avoided.

The manufacture of KCl from *sylvine* (KCl) is very simple; the salt is recrystallized.

Van 't Hoff's Researches on the Stassfurt Deposits.—In the extensive researches of Van 't Hoff and his pupils on the Stassfurt deposits, the solubilities, vapour pressures, etc., of the following systems were investigated:—

(1) $KCl+MgCl_2$ in (*a*) pure water, and (*b*) saturated NaCl solution.

(2) $KCl+MgCl_2+K_2SO_4$ in the same solvents.

Case (1) (*a*).—KCl and $MgCl_2$ in aqueous solution.

Below −12° KCl and $MgCl_2.8H_2O$ or $MgCl_2.12H_2O$ separate. Above 167·5° KCl and $MgCl_2.4H_2O$ or $MgCl_2.2H_2O$ separate. Between the temperature limits −12° and 167·5° carnallite, $KCl.MgCl_2.6H_2O$, may exist as a solid phase in contact with the solution, and for each intermediate temperature there is a certain range of compositions of solutions from which this double salt alone separates. Thus:—

At 25° carnallite separates from a solution—

$$100H_2O+0{\cdot}2KCl+(9{\cdot}9-10{\cdot}5)MgCl_2$$

At 100° carnallite separates from a solution—

$$100H_2O+0{\cdot}4KCl+(10{\cdot}8-14{\cdot}2)MgCl_2$$

If carnallite is treated with pure water it breaks up into solid KCl and a solution containing KCl and $MgCl_2$, and if it is treated with solutions containing varying amounts of KCl and $MgCl_2$ the decomposition proceeds to different extents; at each temperature there are solutions with definite ranges of magnesium chloride content with which carnallite exists unchanged. Thus at 25°, as we have seen, the solutions are—

$$100H_2O + 0{\cdot}2KCl + (9{\cdot}9\text{–}10{\cdot}5)MgCl_2$$

With pure water at 25° carnallite deposits 98 per cent. of its KCl and leaves the solution of the above composition—

$$KCl.MgCl_2.6H_2O + 4H_2O = 0{\cdot}98KCl + 0{\cdot}1(100H_2O + 0{\cdot}2KCl + 9{\cdot}9MgCl_2)$$

On evaporation of the mother-liquor, carnallite alone separates until the solution has passed from the composition of the limiting solution $100H_2O + 0{\cdot}2KCl + 9{\cdot}9MgCl_2$ to the composition of the other limiting solution $100H_2O + 0{\cdot}2KCl + 10{\cdot}5MgCl_2$, at which point magnesium chloride separates along with the carnallite.

If to the solution containing magnesium and potassium chlorides obtained by the action of water on carnallite more magnesium chloride is added, then potassium chloride separates, and with sufficient magnesium chloride the separation is nearly quantitative.

Outside the temperature limits —12° and 167·5° other reactions occur. Thus if carnallite alone is heated to 167·5° it breaks up with deposition of 75 per cent. of its KCl as follows:—

$$KCl.MgCl_2.6H_2O = 0{\cdot}75KCl + (MgCl_2 + 0{\cdot}25KCl + 6H_2O)$$

On cooling the liquid $MgCl_2 + 0{\cdot}25KCl + 6H_2O$ to 116° it deposits solid carnallite and leaves the liquid $MgCl_2 + 0{\cdot}25KCl + 6{\cdot}18H_2O$. In this way there are obtained in one operation from solid carnallite—

75 per cent. of KCl.

75 per cent. of fused $MgCl_2.6H_2O$ containing only 1 per cent. KCl.

25 per cent. of unaltered carnallite.

If the operation is repeated with the unaltered carnallite, only $25 \times 0{\cdot}25 = 6{\cdot}25$ per cent. of the carnallite is left unchanged.

From a mixture of carnallite and $MgCl_2.4H_2O$ at 152·5° there is obtained solid KCl and the liquid $MgCl_2 + 0{\cdot}12KCl + 5H_2O$. If therefore carnallite is first heated to drive off one molecule of water, and is then heated to 152·5°, the reaction

$$\begin{aligned} 2(MgCl_2.KCl.6H_2O) &= MgCl_2.KCl.6H_2O + MgCl_2.KCl.4H_2O \\ &= 0{\cdot}88KCl + (MgCl_2 + 0{\cdot}12KCl + 5H_2O) \end{aligned}$$

occurs. If now the liquid is mixed with one molecule of water and cooled to 116°, practically all the KCl is deposited as carnallite and fused magnesium chloride is left. If these two operations are carried out one therefore obtains 88 per cent. KCl, 88 per cent. fused magnesium chloride, and 12 per cent. unchanged carnallite. By repeating the operations with this carnallite, only $12 \times 0{\cdot}12 = 1{\cdot}44$ per cent. remains unchanged.

The behaviour when potassium sulphate is present is more complicated. On evaporation of a solution containing the three salts: KCl, $MgCl_2$, and K_2SO_4, those salts (including double salts) separate first with respect to which the solution first becomes saturated. Thus at 25°, $MgSO_4.7H_2O$, when no excess of $MgCl_2$ or K_2SO_4 is present. By further evaporation the deposition of this salt continues until saturation with a second salt is reached, the ratio of K_2SO_4 and $MgCl_2$ in the solution of course remaining constant whilst $MgSO_4.7H_2O$ is separating. The second salt to be deposited is the double salt schönite, $K_2SO_4.MgSO_4.6H_2O$. As soon as a second solid phase separates, one of two things may happen:—

(i) The solution may go on depositing the two salts till it is completely evaporated, *e.g.* when $MgSO_4.7H_2O$ and schönite separate together;

(ii) The separation of the second salt involves the disappearance of the first salt in contact with the solution, *e.g.* when K_2SO_4 separates after schönite, or $MgSO_4.7H_2O$ after $MgSO_4.6H_2O$.

A solution of equimolecular amounts of K_2SO_4 and $MgCl_2$ when evaporated at 25°, and the solids separating removed from the solution, deposits the following salts in order :—

K_2SO_4 and schönite ;
KCl and schönite ;
KCl and $MgSO_4.7H_2O$;
KCl and $MgSO_4.6H_2O$;
$MgSO_4.6H_2O$ and carnallite ;
$MgSO_4.6H_2O$, carnallite, and bischoffite ($MgCl_2.6H_2O$).

The behaviour of the solutions of the four salts KCl, K_2SO_4, $MgCl_2$, and $MgSO_4$ saturated in addition with common salt, which may be regarded as approaching the conditions obtaining during the formation of the Stassfurt deposits, is necessarily very complicated. At 25° on evaporation the following salts separate in order :—

NaCl ;
KCl ;
Carnallite, $KCl.MgCl_2.6H_2O$;
Bischoffite, $MgCl_2.6H_2O$;
Magnesium sulphate hexahydrate, $MgSO_4.6H_2O$;
Epsom salt, $MgSO_4.7H_2O$;
Schönite, $MgSO_4.K_2SO_4.6H_2O$;
Glaserite, $K_3Na(SO_4)_2$;
Magnesium sulphate pentahydrate, $MgSO_4.5H_2O$;
Magnesium sulphate tetrahydrate, $MgSO_4.4H_2O$;
Thenardite, Na_2SO_4 ;
Astrachanite, $Na_2SO_4.MgSO_4.4H_2O$.

The salts $Na_2SO_4.10H_2O$ (Glauber salt), and $MgSO_4.Na_2SO_4.2H_2O$ (löweit), were only formed below and above 25° respectively.

The actual behaviour of sea water on evaporation is complicated by the presence of calcium salts and borates ; the influence of these substances was also studied by Van 't Hoff, but for further details the original memoirs must be consulted. The whole series of researches is based on the Phase Rule, which proved a valuable guide in the laboratory. How far such researches could have been carried by a chemist unacquainted with the phase rule, and having no guide to the apparently chaotic results obtained on evaporating mixed salt solutions, it is hard to say. The very meagre results obtained before the problem was taken up by Van 't Hoff would lead one to suppose that little progress could have been made by the older methods of technical investigation, in which the results and guiding principles of modern physical chemistry had no place.

The average composition of the Stassfurt deposits, according to Bischoff, is as follows :—

Rock salt	85·1
Anhydrite	3·7
Polyhalite	0·8
Kieserite	3·3
Carnallite	6·2
Magnesium chloride	0·9

Sodium chloride	85·1
Potassium chloride	1·7
Potassium sulphate	0·2
Magnesium chloride	2·6
Magnesium sulphate	3·1
Calcium sulphate	4·0
Combined water	3·3

The amounts of sodium chloride and calcium sulphate as given are probably too low.

By-products of the Stassfurt Industry.—1. Kieserite, $MgSO_4.H_2O$, is used for making Epsom salts, $MgSO_4.7H_2O$. It is recrystallized from water.

2. Glauber's salt, $Na_2SO_4.10H_2O$, is made to the extent of 10,000 tons per annum by Scheele's process (1787)—

$$2NaCl+MgSO_4+10H_2O=MgCl_2+Na_2SO_4.10H_2O$$

Crystallization is carried out below 0°, in the Rhône district by artificial cold, in Stassfurt during the winter months, in large wooden vats.

3. Magnesium chloride, $MgCl_2$. The final mother-liquors are evaporated to a boiling point of 157°, and on cooling yield a white translucent mass containing about 50 per cent. $MgCl_2$, which corresponds nearly with the hydrate $MgCl_2.6H_2O$. About 12,000–16,000 tons are made annually for use as a thread lubricant in cotton spinning, in calico weaving, for cements, and for the preparation of magnesia for refractories and other purposes (see under Magnesium).

4. Boric acid, H_3BO_3. About 300 tons are made annually from the mineral Boracite, $2Mg_3B_8O_{15}.MgCl_2$, occurring in the Stassfurt deposits.

5. Potash manures. The crude potassium chloride and

sulphate are used directly on the land for manure, especially in the cultivation of sugar beet, which takes up much potash from the soil (see under Vinasse).

6. Bromine is made from the final mother-liquors after the magnesium chloride has been separated. These contain magnesium bromide, $MgBr_2$. They are allowed to trickle down a tower filled with earthenware balls (Fig. 63) into a tank provided with shelves to promote circulation and heated with steam, whilst a current of chlorine gas is passed in the opposite direction, and meets the liquid coming down the tower. Bromine is set free in the form of vapour—

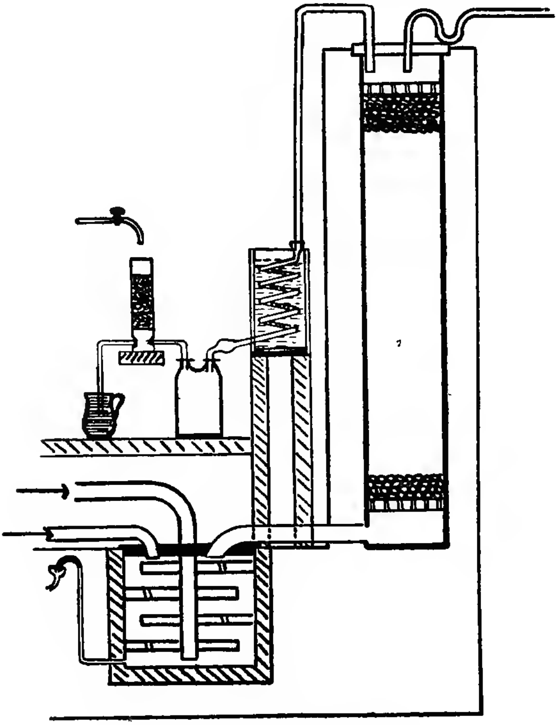


Fig. 63.—Bromine Apparatus.

$$MgBr_2+Cl_2=MgCl_2+Br_2$$

The bromine vapour passes out at the top of the tower, and is condensed in a cooling worm, the last traces being kept back by moist iron turnings in a small tower. The bromide of iron formed in this tower is used to make potassium bromide.

Some bromine is made from the mother-liquor, or *bittern*, of solar salt manufacture by Balard's process. Chlorine is passed in and the liberated bromine shaken out with paraffin oil, which dissolves it and floats on the surface. The oil is then shaken with a solution of caustic soda, which removes the bromine and leaves the paraffin, which is used again. The aqueous layer is evaporated and the sodium bromide decomposed with manganese dioxide and sulphuric acid in retorts, when bromine distils over.

The preparation of bromine from kelp has apparently been abandoned.

Considerable quantities of bromine are made in America. In 1915, the quantity of bromine made in the Ohio River district was 855,857 lbs. Much bromine is present in the Great Salt Lake of Utah in the form of bromides. The American competition has resulted in a considerable lowering in the price of bromine, and is a serious menace to the Stassfurt monopoly.

Other Sources of Potassium Salts.—Besides the Stassfurt deposits, important deposits of potassium salts occur in Alsace and in the north of Spain.

The Alsatian deposits occur near the forest of Monnebruck, at the foot of the now historic Hartmannsweilerkopf, near Mulhouse. They were found in 1904, and are in two layers, the upper 3 ft., and the lower 16½ ft., thick. Their value is estimated at two thousand million pounds, but they are as yet unworked. These deposits are much richer than those at Stassfurt, and it may be anticipated that in the future they will take the place of the German monopoly in supplying a large proportion of the world's markets.

Large deposits of potassium salts have quite recently been discovered at Cardona in the north of Spain, but have apparently been allowed to come under German control. In Eastern Galicia deposits of sylvine and kainite have been discovered, but they have not been worked on account of the competition of Stassfurt. Other large deposits have also been discovered at Elton Lake, on the Ural-Ruizan line.

In America the deposits of Searle's Lake, Nebraska, are rich in potash salts.

An interesting source of potassium salts is found in the fumes emitted from blast furnaces and the furnaces of cement works. These often contain appreciable amounts of potassium salts, and in some steel works, such as the Bethlehem Steel Works in Pennsylvania, these salts are now recovered by scrubbing the exit gases or by electrical precipitation. Whether more potassium salts could be recovered in this way by adding minerals rich in potash but not amenable to direct treatment, such as felspar, is an interesting technical problem.

Potassium Salts from Felspar.—An almost inexhaustible source of potassium salts is found in the primary rocks containing potassium silicate, such as felspar. Felspar itself is very slowly decomposed by atmospheric moisture and carbon dioxide, but the use of finely ground felspar directly as a manure has proved a failure, although supplies are apparently still put on the market by Norwegian firms for that purpose.

Many attempts have been made to obtain potassium salts economically from felspar, and numerous patents have been taken out, but up to the present no successful process seems to have been discovered. Some of the methods proposed are considered below.

1. Ward and Wynants fritted finely ground felspar with lime and fluorspar. The product was lixiviated with water, and the potassium silicate extracted decomposed by carbon dioxide, when silica and potassium carbonate were obtained.

2. Spiller fused the finely ground felspar with a mixture of barium sulphate and coal to a glass, and then extracted with sulphuric acid, when insoluble barium sulphate, which could be used over again, and soluble potassium sulphate were formed.

3. Thompson heated a mixture of 5 parts felspar with

5 parts of nitre cake ($NaHSO_4$) and 1·8 parts of common salt to redness for two to three hours. The residue was ground and lixiviated, and the solution crystallized. The reaction was supposed to consist in the formation of hydrochloric acid from the salt and nitre cake, which with felspar at a high temperature gives potassium chloride. This with the excess of nitre cake gives more hydrochloric acid and potassium sulphate. It is stated that 80–90 per cent. of the potassium can be so recovered.

4. Herstein fuses felspar with calcium chloride and chalk in a revolver, when potassium chloride is volatilized and cement clinker is left. This process is said to produce potassium chloride at a less cost than the Stassfurt salt—presumably only if the " cement " is included.

Potassium Salts.—*Potassium carbonate* is prepared in a variety of ways from the other salts available in larger quantities.

1. From KCl and K_2SO_4 by the Leblanc process. In 1861 Vorster and Gruneberg established a works at Kalk, near Cologne, and other works were afterwards erected in France and Germany, *e.g.* at Croix, near Lille. The charge for the black-ash process is 100 parts K_2SO_4, 80–90 parts of limestone, and 40–50 parts of coal. Batches of 2½–3 cwts. of K_2SO_4 are worked up at a time. KCl is first converted into K_2SO_4 by heating with sulphuric acid as in the salt-cake process.

2. From KCl by the process of Precht :—

$$\underset{\text{solid}}{3(MgCO_3.3H_2O)}+\underbrace{\underset{\text{liquid}}{2KCl}}_{\substack{\text{95 \% saturated}\\ \text{at } 20^\circ}}+\underset{\text{gas}}{CO_2}$$

$$=\underset{\text{solid}}{2(MgCO_3.KHCO_3.4H_2O)}+\underset{\text{liquid}}{MgCl_2}$$

Limekiln gas (30–35 per cent. CO_2) is used ; the solid is separated by suction and boiled with water under pressure at 140°. The following reaction occurs :—

$$\underset{\text{solid}}{2(MgCO_3.KHCO_3.4H_2O)}=\underset{\text{solid}}{MgCO_3}+\underset{\text{liquid}}{K_2CO_3}+9H_2O+\underset{\text{gas}}{CO_2}$$

Potassium carbonate is used in the manufacture of flint glass and hard glass. Bohemian glass, largely used in the manufacture of chemical apparatus, is made by fusing together 50 parts K_2CO_3, 15 parts lime, and 100 parts powdered quartz. Potash glass is less fusible and more resistant than ordinary soda glass. Flint glass, which has a high refractive index and is used in the construction of optical instruments, contains lead oxide in addition to potash.

Caustic potash, KOH, is made in various ways—

1. By causticizing potassium carbonate with lime, as in the usual method for making caustic soda.

2. By electrolysis of potassium chloride solution, as in the electrolysis of brine. 28,000 tons of electrolytic caustic potash were made in Germany in 1903, and used in the manufacture of soft soap, oxalic acid, etc. The power used is 2 kw.-hr. per kilo of KOH. The product when required pure for laboratory purposes (" Pure by alcohol ") is refined by dissolving in alcohol and filtering from K_2CO_3, and evaporating in a silver basin. A similar process is used for obtaining pure caustic soda.

3. From potassium sulphate by direct caustification.

Attempts have been made to obtain caustic potash directly from potassium sulphate (Claussen, 1852) :—

$$K_2SO_4+Ca(OH)_2=CaSO_4+2KOH$$

This avoids preliminary conversion into carbonate, which is a costly process.

The equilibrium is reached sooner than in the carbonate caustification, and the yields are therefore lower. The reaction has been investigated by Herold, who by assuming the solubilities of the two calcium salts as constant, as they are present in the solid phases, obtained the equation of equilibrium—

$$\frac{[OH']^2}{[SO_4'']}=K$$

analogous to the caustification equation of p. 77.

If the dissociation of the calcium salts is assumed to be complete, we have—

$$[Ca^{\cdot\cdot}] = \tfrac{1}{2}[OH'] = S_1$$
$$[Ca^{\cdot\cdot}] = [SO_4''] = S_2$$

and hence—
$$\frac{4S_1^3}{S_2^2} = K$$

The results showed that this equation is followed at low temperatures, but there were deviations at higher temperatures owing to the appearance in the solid phase of the double salt syngenite, $K_2SO_4.CaSO_4.H_2O$. In this case the reaction is—

$$\underset{\text{solid}}{Ca(OH)_2} + H_2O + 2SO_4'' + 2K^{\cdot} = \underset{\text{solid}}{K_2SO_4.CaSO_4.H_2O} + 2OH'$$

Hence we have the equation—

$$\frac{[OH']^2}{[K^{\cdot}]^2[SO_4'']^2} = K\ ;\ [K^{\cdot}] = [SO_4'']$$
$$K = \frac{[OH']^2}{[SO_4'']^4}$$

Thus with increasing concentration of potassium sulphate, increase of caustification results—exactly the opposite result to that occurring in dilute solutions. It was found best to work at low temperatures, say with a saturated solution of potassium sulphate at 0°, when 65 per cent. conversion is obtained. The remaining potassium sulphate can be separated by freezing.

Potassium Bromide and Potassium Iodide.—These two salts are prepared by very similar methods, in one case bromine and in the other iodine being used :—

1. The halogen element is added to a solution of caustic potash, when potassium bromide or iodide, and bromate or iodate, are formed :—

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$$
$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O$$

The solution is evaporated to dryness, a little charcoal is added to facilitate the reduction of the bromate or iodate, and the whole ignited. The bromide or iodide is extracted with water and crystallized.

2. Bromide or iodide of iron, prepared by adding the halogen element to water and iron turnings, is added to a

boiling solution of potassium carbonate, when hydroxide of iron is precipitated and the haloid salt remains in solution—

$$3Fe+4Br_2=Fe_3Br_8$$
$$Fe_3Br_8+4K_2CO_3+4H_2O=8KBr+Fe_3(OH)_8+4CO_2$$

Both potassium bromide and iodide are used in medicine.

Potassium permanganate, $KMnO_4$, is obtained by fusing together a mixture of caustic potash, potassium chlorate, and manganese dioxide. The caustic potash is taken in the form of a saturated solution, and for every ten parts of KOH eight parts of manganese dioxide, and seven parts of potassium chlorate are added. The whole is evaporated to dryness, and fused till the chlorate is decomposed. The dark green mass is lixiviated with water, boiled, and the residue allowed to deposit. The liquid is filtered through asbestos and allowed to stand, when crystals of permanganate separate. Potassium manganate is first formed in the fusion, together with some permanganate, and the manganate is converted into permanganate by the action of water—

$$2KOH+MnO_2+O=K_2MnO_4+H_2O$$
$$3K_2MnO_4+2H_2O=2KMnO_4+MnO_2+4KHO$$

The conversion into permanganate is facilitated by passing carbon dioxide through the solution.

Prolonged fusion in a flat vessel in presence of air may be used instead of adding the chlorate.

Potassium Chromate and Dichromate.—These salts are prepared from native ferrous chromite, or chrome-iron ore, $FeCr_2O_4$, by the process of Stromeyer, which consists in roasting the finely powdered ore with a mixture of lime and potassium carbonate in presence of atmospheric oxygen. A mixture of $4\frac{1}{2}$ parts of ore, $2\frac{3}{4}$ parts of K_2CO_3, and 7 parts of lime is dried and then heated to bright redness with an oxidizing flame, the mass being constantly stirred. The mass is lixiviated, and calcium chromate in the solution decomposed by adding potassium sulphate, when calcium sulphate is precipitated and potassium chromate remains in solution. If dichromate is to be made, the requisite amount of sulphuric acid is added and the solution allowed to cool, when the dichromate crystallises out in red crystals.

$$2FeCr_2O_4+4K_2CO_3+7O=Fe_2O_3+4K_2CrO_4+4CO_2$$
$$2K_2CrO_4+H_2SO_4=K_2Cr_2O_7+K_2SO_4+H_2O$$

Metallic potassium is prepared by electrolysis of caustic potash or by heating the fluoride or silicofluoride with aluminium. Potassium oxide, K_2O, is obtained by heating potassium nitrite with potassium—

$$2KNO_2+6K=4K_2O+N_2$$

Magnesium.—Magnesium and its salts are prepared from the magnesium chloride by-product of the Stassfurt industry (see p. 285).

Metallic magnesium is prepared electrolytically from carnallite at the Hemlingen Works at Bremen, and a small amount at Griesheim. The salt, fused at a temperature a little above its melting-point in a steel crucible which acts as the cathode, is electrolyzed by a current of 1000 amps. per sq. metre at 7–8 volts, with a carbon anode. The anode is surrounded by a porcelain tube and chlorine is led off. During the fusion and electrolysis a mixture of sodium and potassium chlorides is added, so that the composition is constantly—

$$41{\cdot}6MgCl_2+32{\cdot}6KCl+25{\cdot}66NaCl$$

Small spheres of metal separate, which are melted together in a crucible with or without a flux, and cast into bars.

In America an alloy of magnesium and aluminium is first prepared, and the magnesium then separated by distillation.

Magnesium is used as a source of light for special purposes, such as in photography, as a reducing agent in the preparation of boron, etc., mixed with barium peroxide for initiating thermite charges, and in the preparation of organo-metallic compounds in the Grignard reaction. An alloy of 10–20 per cent. magnesium and 80–90 per cent. aluminium forms *Magnalium*, which is very tough and light. The consumption of magnesium is comparatively small.

Magnesium Salts.—The preparation and uses of magnesium chloride, which forms the usual starting-point in the preparation of magnesium salts, have been described already (p. 285).

If a solution of magnesium chloride is precipitated with sodium carbonate, *magnesia alba levis,* $4MgCO_3.Mg(OH)_2.5H_2O$, is formed, which on drying at a low temperature forms a voluminous white powder. When this is heated with water to 100°, *magnesia alba ponderosa,* $MgCO_3.Mg(OH)_2.4H_2O$, which is much denser, is formed, and if this is heated to 300° *calcined magnesia,* or magnesium oxide, is left. These three products are used in medicine, and the oxide is used in making refractory bricks for lining Bessemer converters for the basic steel process. Magnesia bricks are made from dead-burnt magnesite, or native magnesium carbonate, which is crushed and mixed with sufficient gently calcined magnesite to give the mass a plastic consistency. The bricks are fired at a red heat. Materials are also made from magnesia fused in the electric furnace similarly to silica. Magnesia is used together with zirconia and other rare earths in the preparation of rods for the Nernst lamp.

Magnesia alba is also prepared from bittern, or the residue of solar salt manufacture, by precipitating the hydroxide, $Mg(OH)_2$, with lime and then passing carbon dioxide until the magnesium carbonate first produced is redissolved in the form of the bicarbonate. When the solution is heated to the boiling point, magnesia alba is precipitated.

Magnesium sulphate is usually prepared from kieserite by lixiviating out the chlorides of magnesium and sodium with cold water in tanks on sieves, through which the kieserite falls in a fine powder. This is packed in moulds, when it solidifies to a mass of $MgSO_4$, bound together by $MgSO_4.6H_2O$, and contains 80–90 per cent. $MgSO_4$. This is ground and sold. If recrystallized from water it forms Epsom salts, $MgSO_4.7H_2O$. Magnesium sulphate is used in medicine and as a warp-sizing in cotton spinning.

Magnesium peroxide in an impure form is obtained by precipitating a solution of magnesium chloride or sulphate with sodium peroxide. It is used as a mild antiseptic in tooth-powders, etc.

Lithium.—Lithium salts were discovered in 1817 by Arfvedson, and the metal was isolated in 1855 by Bunsen and Matthiessen, who electrolyzed the fused chloride in an iron crucible with a carbon anode and iron cathode.

Lithium occurs in small quantities in siliceous rocks composed of silica, alumina, and alkali metals, notably in *lepidolite*, or lithia-mica, *petalite, spodumene*, and *triphylene*, which contain from 3 to 6 per cent. Li_2O. The lithium salts are extracted from these minerals in various ways :—

(1) Fusion with barium carbonate and sulphate, when barium silicate and the sulphates of the alkali-metals are produced. The solution in water is precipitated with barium chloride, and the alkali-chlorides in the filtrate evaporated to dryness and treated with a mixture of absolute alcohol and ether, in which only lithium chloride, $LiCl$, dissolves (Troost).

(2) Digestion of the finely powdered mineral with concentrated hydrochloric or sulphuric acid. Silica is rendered insoluble, and the solution, after precipitation with sodium carbonate to remove iron, alumina, magnesia, etc., is concentrated by evaporation, and *lithium carbonate*, Li_2CO_3, precipitated with sodium carbonate.

Lithium salts also occur in radioactive minerals, such as carnotite, in sea water, and in the waters of many mineral springs (*e.g.* the water of the Wheal-Clifford spring, near Redruth in Cornwall), and in plant ashes.

Lithium hydroxide, $LiOH$, is prepared by boiling a solution of lithium carbonate with lime or baryta. It is a strong alkali. It crystallizes from dilute alcohol as $LiOH.H_2O$.

Lithium chloride below 15° forms a hydrate, $LiCl.2H_2O$; above 15° it crystallizes anhydrous. It is very deliquescent.

Lithium sulphate, Li_2SO_4, is soluble in alcohol and in water.

Lithium carbonate, Li_2CO_3, is insoluble in absolute alcohol, and only sparingly soluble in water, being more soluble in the cold. It dissolves in a solution of carbon dioxide, forming a bicarbonate $LiHCO_3$. The commercial carbonate usually contains about 98·5 per cent. Li_2CO_3. Organic lithium salts (*e.g.* lithium salicylate) are used in pharmacy, as a cure for gout and other complaints.

Salts of cæsium and rubidium are exceedingly scarce, and are not prepared industrially.

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